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АКАДЕМИИ НАУК СССР

PROCEEDINGS of the ACADEMY of SCIENCES of the USSR

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Section: CHEMISTRY

Volume 110, Issues 1-6

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IN ENGLISH TRANSLATION

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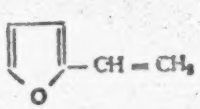
SYNTHESIS AND POLYMERIZATION OF VINYL DERIVATIVES OF THE FURAN AND THIOPHENE SERIES

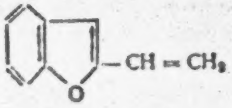
I.V. Andreeva and M.M. Koton

(Presented by Academician V.A. Kargin, March 28, 1956)

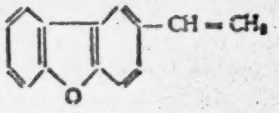
Vinyl derivatives of the furan and thiophene series have been little studied up to the present time. Moreover, there are literature data, chiefly patent, indicating that many of their polymers have high softening points and good dielectric properties. The investigation of these compounds is also of independent interest, since it permits the study of the effect of the nature of different heterocyclic substituents in the ethylene molecule on the properties of the polymers obtained. We set ourselves the problem of studying the effect of increasing the number of condensed benzene rings in vinyl derivatives of the furan and thiophene series on polymerizability and on the properties of the polymers obtained. It was also of interest to examine the effect of the substitution of an oxygen atom by a sulfur atom on the properties of these polymers. With this aim, the following were synthesized in the furan series:



2-vinylfuran

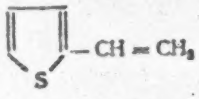


2-vinylbenzofuran

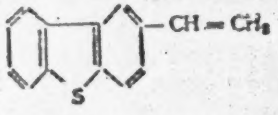


2-vinyldibenzofuran

And in the thiophene series:



2-vinylthiophene



2-vinyldibenzothiophene

Vinylfuran and its polymers are the most studied of these monomers and polymers [1,2]. The literature [3-7] gives mainly technical characteristics for the rest of the polymers. It should be noted that a comparison of the properties of the monomers and polymers and likewise a study of the polymerization kinetics of these monomers have not been carried out up to the present.

The monomers were synthesized by the following method:

Vinylfuran was prepared by decarboxylation of furylacrylic acid, which, in turn, was prepared by Perkin's reaction of furaldehyde.

Vinylthiophene was prepared by condensation of thienylmagnesium iodide with ethylene oxide and subsequent dehydration of the resulting carbinol over solid potassium hydroxide.

The vinyl derivatives of benzofuran, dibenzofuran, and dibenzothiophene were prepared by a general method. The corresponding ketones were reduced by Meerwein-Ponndorf reduction to the carbinols which were subsequently dehydrated in the vapor phase over aluminum oxide. Methylbenzofuryl ketone was not prepared by direct acetylation by Friedel-Crafts reaction, as were the other ketones, but by ring closure during condensation of salicyl aldehyde with chloroacetone. The original condensed systems were not available, and were synthesized: dibenzofuran

TABLE 1

Physicochemical Properties of the Monomers

Monomer	B.p., °C, and pressure, mm Hg			Mp, °C		n_D^{20}		Elemental composition, %			
	Found	Lit. data		Found	Lit. data	Found	Lit. data	C		H	
								found	calc.	found	calc.
2-Vinylfuran	96—97/764 32.1.6 · 10⁻¹ 117/2; 120/0.5 66.5/18	95—101 72/2 141.1; 197/2; 124/1.8 63.5/30; 66.5/18		Liquid " 31 Liquid	Liquid " 30 · 34—39 Liquid	1.4914(25°) 1.4920(25°) 1.6372(20°) 1.5722(20°)	1.5053(25°) 1.6125(25°) 1.6320(20°) 1.5612(25°) 1.6007(25°) 1.5720(20°)	76.36 82.13 86.59 83.41	76.33 82.33 86.34 83.13	6.33 5.72 5.14 5.32	6.25 5.41 5.43 5.13
2-Vinyldibenzothiophene	167/0.5**	None		43	43	Solid	Solid	80.52	80.90	5.09	4.78

*No analytical data on double bonds in the literature.

**Polymerized during distillation at 0.5 mm.

from phenol, and dibenzothiophene from diphenyl and sulfur, in the presence of aluminum chloride. Purification of the liquid monomers was carried out by repeated vacuum distillation and crystallization by alternating vacuum distillation and crystallization by freezing. Vinylfuran was distilled over solid caustic potash [potassium hydroxide], which made it possible to obtain the monomer in a high degree of purity. The purity of the monomers prepared can be judged from the data from elemental and double bond analyses which are presented in Table 1.

The vinyldibenzothiophene had a purity of 96-98% owing, apparently, to its high polymerizability. The preparation of the monomers in a high degree of purity made it possible to improve the accuracy of the available physicochemical constants of the monomers and to determine the previously unknown constants (see Table 1).

Polymerization processes proceeding both by a free radical mechanism (mass, solution, and emulsion polymerization) and by an ionic mechanism were investigated in the present work. Polymerization kinetics were studied dilatometrically with 0.5 mole % benzoyl peroxide in mass and solution polymerizations at 60, 80, 90, and 100°, and also in the presence of butyllithium at 35° and boron trifluoride etherate at 0°.

The effect of molecular oxygen on the polymerization process was established by a series of preliminary experiments on benzoyl peroxide-catalyzed polymerization, and, as a result of this, further experiments were carried out under conditions of most complete exclusion of atmospheric oxygen, thereby permitting closely reproducible results to be obtained. A parallel investigation of mass and solution polymerization processes was carried out, because some of the monomers were liquid and others were crystalline.

A mercury dilatometer of special construction was used for the investigation of the kinetics of benzoyl peroxide-catalyzed mass polymerization. In the investigation of the kinetics of solution polymerization catalyzed by benzoyl peroxide, butyllithium, or boron trifluoride etherate, the reaction tubes were filled by means of a special filling apparatus. In those cases where an ionic-type catalyst was used, the dilatometer reaction tube consisted of two sections, one of which was filled with monomer and solvent using the special apparatus, and the other was filled with catalyst using a Schlenk apparatus.

The investigation of the kinetics of the benzoyl peroxide-catalyzed polymerization process at different temperatures made it possible to calculate the activation energy. The following values were obtained for monomers of the furan series: vinylfuran, 17 ± ± 1.0 kcal/mole; vinylbenzofuran, 16.5 ± 0.5 kcal/mole; vinyldibenzofuran, 12.4 ± 0.5 kcal/mole.

Comparing the rate data from free radical-catalyzed polymerizations of monomers of the furan series, both in mass for vinylfuran and vinylbenzofuran at 80 and 100° (Figure 1) and in solution at 100° for vinylfuran, vinylbenzofuran, and vinyldibenzofuran (Figure 2), it is seen that the polymerization rate increases with an increase in the number of condensed rings in the monomer. We were

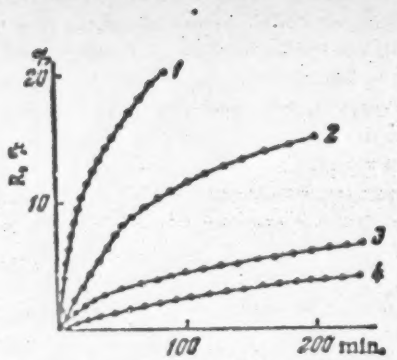


Fig. 1. Kinetics, R, of the mass polymerization of vinylfuran and vinylbenzofuran with 0.5 mole % benzoyl peroxide. 1) VBF at 100°; 2) VBF at 80°; 3) VF at 100°; 4) VF at 80°.

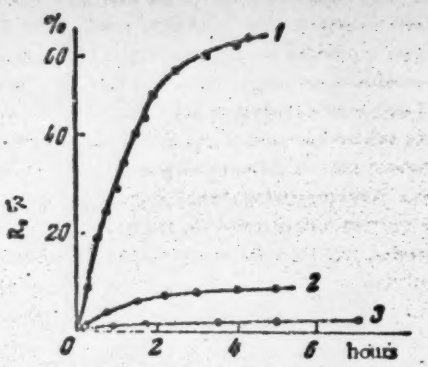


Fig. 2. Kinetics, R, of the polymerization of vinyl derivatives of the furan series in 1 M toluene solution with 0.5 mole % benzoyl peroxide at 100°. 1) VDBF; 2) VBF; 3) VF.

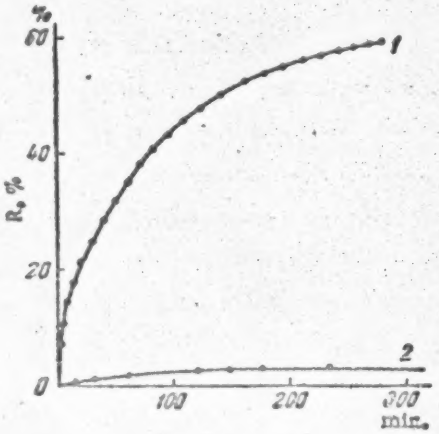


Fig. 3. Kinetics, R, of the polymerization of monomers of the thiophene series in 1 M toluene solution with 0.5 mole % benzoyl peroxide at 100°. 1) VDBT; 2) VT.

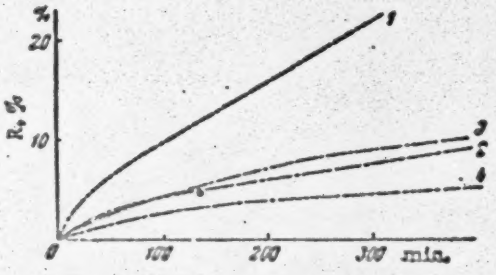


Fig. 4. Kinetics, R, of the mass polymerization of vinylfuran and vinylthiophene catalyzed with 0.5 mole % benzoyl peroxide. 1) VT at 100°; 2) VF at 100°; 3) VT at 80°; 4) VF at 80°.

led to this same conclusion by a study of the polymerization kinetics of these same compounds proceeding by an ionic mechanism. An investigation of the rate of the benzoyl peroxide-catalyzed mass polymerization of vinylthiophene at different temperatures made possible the calculation of the activation energy, which was 16.0 ± 0.5 kcal/mole.

On comparing the polymerizability of monomers of the thiophene series by means of the polymerization rates (Figure 3), it is seen that vinyldibenzothiophene polymerizes at a considerably higher rate than vinylthiophene.

The investigations carried out with monomers of the furan and thiophene series makes it possible to compare the analogous monomers and to examine the effect of the substitution of an atom of sulfur for an atom of oxygen both on polymerizability and on the properties of the polymers obtained. Thus, from the rates of the benzoyl peroxide-catalyzed mass polymerizations (Figure 4) it is seen that vinylthiophene is more reactive than vinylfuran. The per cent conversion of vinylthiophene is approximately twice that of vinylfuran at equal time intervals. The same tendency is observed on comparison of the three-ring representatives of the series investigated, vinyldibenzofuran and vinyldibenzothiophene. However, in this case, this effect is present to a lesser extent, apparently owing to the complexity of the molecules.

Thus, with an increase in the number of condensed rings in the monomer molecule, the rate of the polymerization process increased both in the furan series and in the thiophene series. Substitution of an atom of sulfur for the oxygen atom increases the polymerization rate of analogs.

Besides investigations of polymerization kinetics and with the aim of studying the properties of the polymers obtained, we conducted experiments on mass polymerizations with a step-wise increase in temperature and with various initiators. When the polymerizations were carried out with free radical-type initiators, the dielectric properties and the softening points of the polymers were maintained almost without change. It can be seen from the intrinsic viscosities that polymers of vinyldibenzofuran were of higher molecular weight than polymers of vinylbenzofuran (for polyvinyldibenzofuran $[\eta] = 0.2-0.6$, and for polyvinylbenzofuran $[\eta] = 0.1-0.2$). The molecular weight of the polymer depends not only on the nature of the monomer, but on the reaction conditions and on the nature of the initiator used. Thus, comparatively higher molecular weight products were obtained from both vinylbenzofuran and, especially, vinyldibenzofuran when azobisisobutyronitrile was the initiator. Higher molecular weight products were obtained also during thermal polymerization carried out under the same conditions in the absence of atmospheric oxygen. However, the high molecular weight polymers had the same softening point and the same dielectric properties as the comparatively low molecular weight polymers. It was established that the softening point of the polymers increased with an increase in the number of condensed benzene rings in the monomer molecule. Sulfur-containing polymers had softening points somewhat higher than the corresponding furan derivatives. The dielectric properties were also improved with an increase in the number of benzene rings. They were better for the sulfur-containing analogs, apparently because of the lower polarity of the compounds containing a sulfur atom in comparison with the compounds containing an atom of oxygen. This difference was less for the higher representatives of these series.

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Institute of High Molecular Compounds
Academy of Sciences, USSR

CATALYTIC DEMETHYLATION OF α-PICOLINE TO PYRIDINE BY MEANS OF STEAM

Academician A.A. Balandin, L.I. Sovalova and T.A. Slovokhotova

The preparation of pyridine and its homologs is of practical interest. Three methods for the demethylation of α-picoline have been patented: pyrolysis of α-picoline at 800° in a stream of hydrogen containing hydrogen sulfide gives a pyridine yield of 21% [1]; catalytic oxidation with air at 580° over a catalyst of vanadium oxide and molybdenum oxide on pumice gives a pyridine yield of 15.3% [2]; cracking over silica-alumina catalyst (90% SiO_2 and 10% Al_2O_3) at 450° and 150 atm. gives 11.1% pyridine and 16.4% di- and polymethylpyridines [3].

Previous work in our laboratory established that demethylation of aromatics proceeds smoothly in the presence of water over a catalyst of nickel on aluminum oxide at temperatures of 300-400°. Thus, toluene yields benzene [4], and xylenes yield toluene and benzene [5]. Destruction of aromatic rings is incomplete, and by selection of reaction conditions (catalyst composition and method of preparation, molar ratio of water to hydrocarbon, temperature) such destruction can be held to a minimum.

In the present work a new method for the demethylation of α-picoline to pyridine is proposed and investigated, in which the demethylation is accomplished by means of steam in the presence of a catalyst of nickel on aluminum oxide.

In the range 148-425° and at molar ratios of water: α-picoline = 22:219, liquid and gaseous products contain C_5H_5N, NH_3, CO_2, CO, H_2, and CH_4. Appreciable coke deposition on the catalyst was not observed. Table 1 shows variation, with temperature, in amount of α-picoline reacted at a molar ratio of water: α-picoline = 22:1. Reaction began at ~150°; above 400° the rate became considerable. Pyridine yield was 50% on α-picoline at 415° and a molar ratio of water: α-picoline = 22:1.

TABLE 1

Temp., °C	Amount of α-picoline reacted in % of that charged			Pyridine yield	Amount of α-picoline totally destroyed
	Total	Forming pyridine	Ring destruction	In % of α-picoline reacted	
148	0.5				
318	4.7	4.5	0.2	95.75	4.25
415	60	50	10	83.3	16.7

TABLE 2

Mole ratio water: α-picoline	Amount of α-picoline reacted in % of that charged			Pyridine yield	Amount of α-picoline totally destroyed
	Total	Forming pyridine	Ring destruction	In % of α-picoline reacted	
22	60	50	10	83.3	16.7
59	46.6	38.5	8	82.8	17.2
155	22.1	16.8	3.5	84.3	15.7
153	22.2	18.7	3.5	84.2	15.7
219	18.5	16.0	2.5	86.5	13.5

The reaction slowed down with an increase in the amount of water. In Table 2 is shown the variation in the amount of α-picoline reacted at 415° to yield pyridine and the amount reacted with complete destruction with the molar ratio of water to α-picoline.

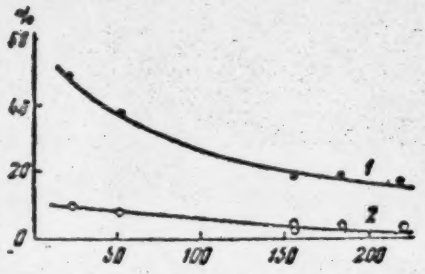


Fig. 1. Variation in the yield of pyridine (1) and ammonia (2), in % of α-picoline charged, with molar ratio of water to α-picoline at a temperature of 415°.

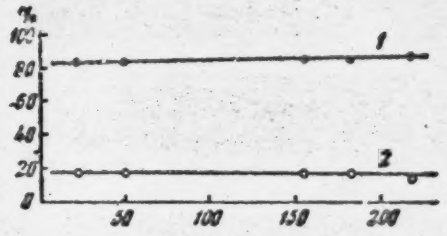


Fig. 2.. Variation in the yield of pyridine (1) and ammonia (2), in % of α-picoline reacted, with molar ratio of water to α-picoline at a temperature of 415°.

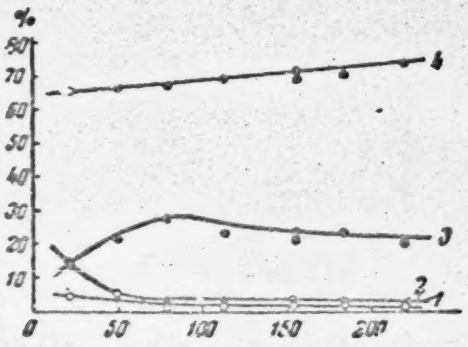


Fig. 3. Variation in the composition of gaseous products, in % with molar ratio of water to α-picoline at a temperature of 415°. 1) CH_4; 2) CO; 3) CO_2; 4) H_2

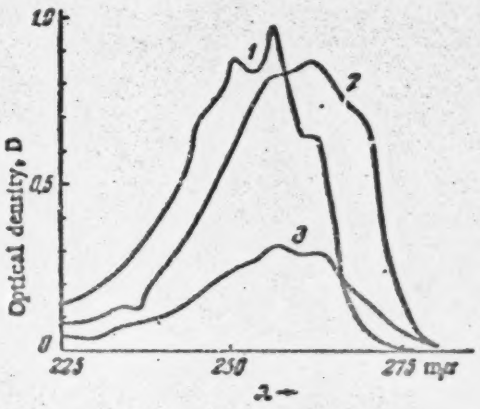


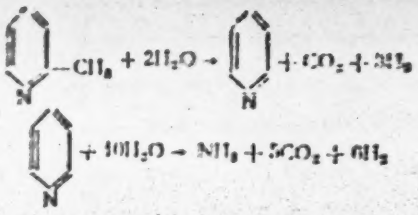
Fig. 4. Absorption spectra: 1) pyridine; 2) α-picoline; 3) mixture of pyridine and α-picoline containing 50% pyridine.

The variation in product distribution with molar ratio of water to α-picoline is shown in Figures 1-3. Within the limits of the molar ratios tested, the yield of pyridine decreased with an increase in the amount of water. The content of ammonia in the catalyzate, which resulted from the complete destruction of the pyridine nucleus, also decreased. The content of hydrogen, produced by the reaction with water, increased continuously with an increase in the amount of water. The amount of carbon dioxide at first increased, and then slowly decreased.

Thus, an increase in the concentration of water in the reaction mixture slows down both the reaction resulting in the complete destruction of the pyridine nucleus and the demethylation reaction. Within the limits of molar ratios of water to α-picoline tested, this ratio remains approximately constant at a value of 5 (Figure 2), but it is strongly temperature dependent.

Judging from the results of the analyses of the gaseous products and catalyzate, under the conditions used the nitrogen of the pyridine ring is not oxidized either to oxides or to free nitrogen; rather, it only undergoes hydrogenation to ammonia. Methane formation is also depressed by water. To a slight degree, the reaction with water also proceeds with the formation of carbon monoxide.

From the above, it follows that, under our conditions, the following basic reactions proceed:



EXPERIMENTAL

The experiments were carried out in a catalytic apparatus with a detachable reactor previously described by one of the present authors [6]. The catalyst, nickel on aluminum oxide in a ratio of 1:1, was prepared and reduced by the method of N.D. Zelinsky [7], and was afterwards heated in a stream of hydrogen at 700°, since, according to literature data [8] and our data [4], such heat treatment increases the activity of the catalyst in the reaction of hydrocarbons with water. Before an experiment, the catalyst was prereduced for one hour at the temperature of the experiment and flushed with nitrogen, and at the conclusion of the experiment it was removed from the hot furnace in a stream of nitrogen and kept covered, since it was previously shown by us that cooling of the catalyst in a moist atmosphere leads to a sharp decrease in its activity [9]. The original α-picoline was distilled in a column of 37 theoretical plates; it had the following constants: b.p. 128.8°; n_D^{24} 1.5015 (literature data: b.p. 128.8°; $n_D^{16.7}$, 1.5029; $n_D^{17.1}$, 1.5024).

The gas was collected, and its rate was recorded automatically with a UGSP gas meter. The gas rate was constant over the interval of an experiment, and was reproducible. This indicates constant catalyst activity under the working regime described above. The gas was analyzed in a VTI apparatus. The ammonia was back titrated with acid. The content of pyridine and α-picoline in the liquid catalyzate was determined by absorption spectra in the ultraviolet region. The analysis was carried out on an SF-4 visual spectrophotometer.

Information is available in the literature on the analysis of mixtures of pyridine and α-picoline with a Beckman spectrograph in the near ultraviolet region [10]. Heptane was used as the solvent. The concentration of pyridine bases was $2\text{-}4 \cdot 10^{-4}$ mole/liter; the sample thickness was 1 cm. In order to calculate concentrations, the optical densities of the solutions were measured at wave lengths of 242.5, 253.5, 262.0, and 268.0 mμ.

It has been reported in other papers that the absorption curves of pyridine and α-picoline in alcohol have the following extremes: 247 mμ (inflection), 251, 257, and 263 mμ (maxima) for pyridine, and 256, 262, and 269 mμ (maxima) for α-picoline [11], and that the sharpness of the maxima increases with an increase in the polarity of the solvent; in addition, the maxima themselves are somewhat displaced in the direction of longer wave length [12].

Since the liquid catalyzate in our experiments was a solution of pyridine bases in water, aqueous solutions having a concentration of $2\text{-}5 \cdot 10^{-4}$ mole/liter were used in taking the spectra. The sample thickness was 1 cm of solution. Standard solutions of pyridine and α-picoline in water had the following extremes: - pyridine 247.5 mμ (inflection), 254 and 261 mμ (minima), 250, 256, and 262.5 mμ (maxima); α-picoline 256 and 268 mμ (inflections), 262 mμ (maximum).

Unknown concentrations of pyridine and α-picoline were calculated from the optical densities at wave lengths of 256 and 262 mμ, the points of the highest absorption maxima of these compounds. Absorption curves for pyridine, α-picoline, and diluted aqueous catalyzate containing 50% pyridine are presented in Figure 4.

The aqueous solution of pyridine bases obtained from the reaction were saturated with potash and the layer of bases separated and dried. The unreacted α-picoline was distilled in a column, following which it had the same constants as the original. The pyridine and α-picoline contained in the lower fractions were separated and identified in the form of their dimercury salts: $C_5H_5N \cdot HCl \cdot 2HgCl_2$, m.p. 176° (literature data, m.p. 177°); $C_6H_7N \cdot HCl \cdot 2HgCl_2$, m.p. 155° (literature data, m.p. 154°).

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M.V. Lomonosov Moscow State University

COMPLEX COMPOUNDS OF DIVALENT PLATINUM WITH γ-AMINOBUTYRIC ACID

L.M. Volshtein and M.F. Mogilevkina

(Presented by Academician P.I. Chernyaev, March 19, 1956)

We recently reported on the preparation of compounds of divalent platinum (Pt^{+2}) with β-aminopropionic acid; in particular, the inner-complex salt $[Pt(NH_2CH_2CH_2CO_2)_2]$ which contains a six-membered ring, was synthesized. It was of interest to attempt to prepare compounds with γ-aminobutyric acid, $NH_2CH_2CH_2CH_2CO_2H$ (denoted below by γH).

It is known that L.A. Chugaev [2] stated that it is impossible to prepare inner-complex salts of chromium with β- and γ-amino acids. We have shown that, by the action of a base on acyclic compounds with β-alanine (denoted by βH) of the composition $[Cr(\beta H)_2Cl_2]$ and $[Pt(\beta H)_2Cl_2]$, inner-complex salts of both chromium [3] and Pt^{+2} [1] can be precipitated. Therefore, we set ourselves the problem of studying the acyclic compound $[Pt(\gamma H)_2Cl_2]$ and of treating it with base.

The compound $[Pt(\gamma H)_2Cl_2]$ was successfully synthesized, but the action of a base on it showed that closure of seven membered rings through the γ-aminoacid does not occur, and the inner-complex salt is not formed. Starting with $[Pt(\gamma H)_2Cl_2]$, other acyclic compounds were prepared, the compositions of which included the molecules $\gamma H([Pt(\gamma H)_2(NH_3)_2]Cl_2$ and $[Pt(\gamma H)_2(ThiO)_2]Cl_2$ (where ThiO = CSN_2H_4), or the radical $NH_2(CH_2)_2CO_2^-$ with a closed ring, the compounds being denoted below by $\gamma([Pt\gamma_2(NH_3)_2]$ and $[Pt\gamma_2(ThiO)_2])$.

It was of interest to compare the complex-forming abilities of α- and γ-aminobutyric acids*. In contrast to γH, α-aminobutyric acid, $CH_3CH_2CH_2CH(NH_2)CO_2H$ (denoted by MH), yields an inner-complex compound with a five-membered ring and having the composition $\left[Pt\left(\langle\!\rangle\!\!\begin{matrix}NH_2\\CO\end{matrix}\!\!\rangle CHCH_2CH_2CH_3\right)_2\right]$. However, the acyclic compounds with γH, for example $[Pt(\gamma H)_2(NH_3)_2]Cl_2$, proved to be considerably more stable than the analogous (and isomeric) compounds with MH, for example $[Pt(MH)_2(NH_3)_2]Cl_2$.

EXPERIMENTAL

To 4 mmoles of K_2PtCl_4 and 16 mmoles of γH was added 15 mmoles of KOH in the form of a 1.8 M solution. The solution was heated on a water bath for 20 minutes. After heating for 5 minutes, the solution became almost colorless. Neither reduction of the platinum nor the formation of any insoluble complexes was observed. 20 ml of concentrated HCl was then added, and the mixture was heated on a water bath for several hours. After one hour, precipitation of light yellow, lamellar crystals began. The amount of precipitate slowly increased; the yield exceeded 75%. The precipitate was filtered by suction, washed with dilute HCl, alcohol, and ether, and dried at 105°. The composition of the compound corresponded to the formula $[Pt(NH_2CH_2CH_2CH_2CO_2H)_2Cl_2]$ (denoted below by γ-dichloride).

Found %: Pt 41.27; 41.39; Cl 15.12; N 6.04; H^+ 0.45. $[Pt(\gamma H)_2Cl_2]$. Calculated %: Pt 41.33; Cl 15.01; N 5.93; H^+ 0.427.

*The compounds of α-aminobutyric acid were prepared by one of us together with N.S. Velikanova.

The γ-dichloride is difficultly soluble in water, but a 2-hour extraction with water gave a $5 \cdot 10^{-4}$ M solution. In conformity with the coordination formula of the compound, the solution has an acid reaction toward methyl red, and $AgNO_3$ produces an opalescence which changes into a precipitate on boiling.

On heating K_2PtCl_4 with γH in alkaline solution, a reaction occurs, apparently according to:

$$K_2PtCl_4 + 4\gamma H + 4KOH \rightarrow K_2[Pt\gamma_4] + 4KCl + 4H_2O.$$

With the addition of acid, $K_2[Pt\gamma_4]$ is converted into $[Pt(\gamma H)_4]Cl_2$, which undergoes Jörgensen cleavage slowly on heating with the formation of γ-dichloride. A similar mechanism was demonstrated in the case of the preparation of the analogous β-alanine dichloride which resulted in the isolation of the compound $[Pt(NH_2CH_2CH_2CO_2H)_4]Cl_2$. If the γ-dichloride is formed similarly, it must have a trans-configuration. This was confirmed by the thiourea reaction of N.S. Kurnakov. On warming with excess ThiO, the γ-dichloride went into solution from which a white dithio derivative having the composition $[Pt(NH_2CH_2CH_2CH_2CO_2H)_2(ThiO)_2]Cl_2$ was precipitated by the addition of excess concentrated HCl. This compound was quantitatively titrated with base. After the addition of two equivalents of base, a white precipitate was formed which was very slightly soluble in water and which was a non-electrolyte of the composition $[Pt(NH_2CH_2CH_2CH_2CO_2)_2(ThiO)_2]$, $2H_2O$. The analyses and properties of both thio derivatives corresponded to the formulas given.

Found %: Pt 31.15; 31.65; Cl 11.66; N 13.38; H^+ 0.315. $[Pt(\gamma H)_2(ThiO)_2]Cl_2$. Calculated %: Pt 31.26; Cl 11.35; N 13.45; H^+ 0.32.

Found %: Pt 33.54; 32.93; N 14.02. $[Pt\gamma_2(ThiO)_2]$. $2H_2O$. Calculated %: Pt 33.22; N 14.30.

A treatment of γ-dichloride with base was carried out by titration with an 0.1 M solution of KOH in the presence of phenolphthalein. After the addition of two equivalents of KOH, the γ-dichloride disappeared forming a yellow solution. The solution remained yellow and a precipitate had not formed after standing for many weeks. Now it is known that after back titration of similar dichlorides of the general formula $[Pt(AH)_2Cl_2]$, where AH is an amino acid (MH, glycine [4], α-alanine [5], or tyrosine [6]) or βH [1], the yellow solution gradually decolorizes in the cold, and an inner-complex salt is precipitated. In particular, 3 days after neutralization of $[Pt(MH)_2Cl_2]$ an inner-complex salt is formed in the cold with a yield of ~45%, and the yield of $[PtM_2]$ approaches 100% on longer standing. In the case of the γ-dichloride, ring closure did not occur, and an inner-complex salt was not obtained. The acyclic compound $K_2[Pt\gamma_2Cl_2]$ apparently remains in the solution. The addition to the solution of 0.1 M HCl in an amount equivalent to the previously added base led to the precipitation of the original γ-dichloride:

$$K_2[Pt\gamma_2Cl_2] + 2HCl \rightarrow 2KCl + [Pt(\gamma H)_2Cl_2].$$

We added the HCl immediately after the back titration, after 10 days, and even after 1 month. In all cases, the original γ-dichloride was precipitated (found %: Pt 41.87, 41.69, and 41.43; calculated %: Pt 41.33) in high yield (~70%) which did not decrease appreciably upon lengthy standing of the neutralized solution. Heating of the neutralized solutions of $[Pt(AH)_2Cl_2]$ considerably accelerates the formation of inner-complex salts. Meanwhile, in the case of $[Pt(\gamma H)_2Cl_2]$, the inner-complex salt was not obtained even after heating. Subsequent addition of HCl in this case led to the precipitation of the original γ-dichloride (found %: Pt 41.21; calculated %: Pt 41.33).

The absence of a tendency toward ring closure by γ radicals is strikingly illustrated by a comparison of the molar conductivities, μ, of solutions of $[Pt(\gamma H)_2Cl_2]$ and $[Pt(AH)_2Cl_2]$ on standing for a long time. In $1 \cdot 10^{-3}$ M solutions of $[Pt(AH)_2Cl_2]$ formed from α- and β-amino acids, μ increases considerably with time, an effect which is dependent on gradual closure of rings:

$$[Pt(AH)_2Cl_2] \rightleftharpoons [PtA_2] + 2HCl.$$

In particular, the inner-complex salt $[PtM_2]$ gradually precipitates in the cold from a $1 \cdot 10^{-3}$ M solution of $[Pt(MH)_2Cl_2]$. If ring closure proceeded irreversibly, 2 mmol. of HCl would be formed per mmol. of $[Pt(AH)_2Cl_2]$ and μ of the solutions, referred to the original concentration of the dichlorides, would reach a value of ~890 ohm^{-1} cm^2 at 25°. In actuality, in $5 \cdot 10^{-4}$ to $1 \cdot 10^{-3}$ M solutions of dichlorides formed from α-alanine [5], tyrosine [6], and MH, μ attains values of 735, 785, and 740 ohm^{-1} cm^2 respectively after standing

for 5-10 days, and it attains a value of 670 ohm^{-1} cm^2 in solutions of $[Pt(\beta H)_2Cl_2]$. Meanwhile, even after lengthy standing of a $2 \cdot 10^{-4}$ M solution of γ-dichloride μ does not exceed 400 ohm^{-1} cm^2. The steady state value of μ is determined by the reaction

$$[Pt(\gamma H)_2Cl_2] + 2H_2O \rightarrow [Pt(\gamma H)_2(H_2O)_2]^{2+} + 2Cl^-$$

and by the partial splitting off of H^+ from the coordinated molecule of γH.

By heating the γ-dichloride with concentrated ammonia, we obtained a non-electrolyte of the composition $[Pt(NH_2CH_2CH_2CH_2CO_2)_2(NH_3)_2]$, which was a white material, very slightly soluble in water. Upon the addition of HCl the material at first went into solution, but after the addition of an excess of concentrated HCl and cooling a white precipitate was formed. The precipitate was filtered by suction, washed with HCl (1:1), alcohol, and ether, and dried at 105-110°. Analysis showed that this compound had the composition $[Pt(NH_2CH_2CH_2CH_2CO_2H)_2(NH_3)_2]Cl_2$.

Found %: Pt 38.61; N 11.29; H^+ 0.39. $[Pt(\gamma H)_2(NH_3)_2]Cl_2$. Calculated %: Pt 38.55; N 11.07; H^+ 0.398.

The compound was readily soluble in water, difficultly soluble in HCl. Upon back titrating there was again formed a white precipitate of the non-electrolyte $[Pt\gamma_2(NH_3)_2]$ (found %: Pt 44.81; calculated %: Pt 45.17). μ of a $1 \cdot 10^{-3}$ M solution of $[Pt(\gamma H)_2(NH_3)_2]Cl_2$ at 25° was 305 ohm^{-1} cm^2. The conductivity was dependent both on the ions $[Pt(\gamma H)_2(NH_3)_2]^{+2} + 2Cl^-$, and on a partial splitting out of H^+ from the coordinated molecules of γH. It is characteristic that μ of solutions of $[Pt(\gamma H)_2(NH_3)_2]Cl_2$ remain constant with time and do not decrease even after boiling of the solutions. Meanwhile, μ of solutions of analogous compounds of α-aminobutyric acid and of α-alanine [5] slowly decrease with time and drop sharply after boiling of the solutions. Both decreases are dependent on conversion of the compound $[Pt(AH)_2(NH_3)_2]Cl_2$ to $[PtCl_2(NH_3)_2]$ – a chloride of the second base of Reise. Thus, for example, a $1 \cdot 10^{-3}$ M solution of $[Pt(MH)_2(NH_3)_2]Cl_2$, which had a μ at 25° of 570 ohm^{-1} cm^2, was subjected to a 10-minute boiling; after cooling to 25°, the solution had a μ of 135 ohm^{-1} cm^2. A similar phenomenon was observed for the analogous α-alanine compound [5]. The absence of a drop in the μ of solutions of $[Pt(\gamma H)_2(NH_3)_2]Cl_2$ after boiling shows that the molecules of γH are bound to the Pt^{+2} more strongly than are molecules of α-amino acids. Boiling of $[Pt(\gamma H)_2(NH_3)_2]Cl_2$ with concentrated HCl leads to this same conclusion. As is well known [4,5], boiling with HCl of the compound $\begin{bmatrix} NH_3 & AH \\ & Pt \\ AH & NH_3 \end{bmatrix} Cl_2$, where AH is glycine or α-alanine, leads to the chloride of the second base of Reise, which is obtained in good yield. The same thing occurs on boiling the compound $\begin{bmatrix} NH_3 & MH \\ & Pt \\ MH & NH_3 \end{bmatrix} Cl_2$ with HCl. In all of these cases cleavage occurs so that chlorine atoms replace molecules of the α-amino acids, which are more weakly bound to the Pt^{+2} than are the molecules of NH_3. Meanwhile, on boiling $\begin{bmatrix} NH_3 & \gamma H \\ & Pt \\ \gamma H & NH_3 \end{bmatrix} Cl_2$ with HCl a mixture of both theoretically possible cleavage products was obtained, that is, a mixture of γ-dichloride and $[PtCl_2(NH_3)_2]$. We titrated this mixture with 0.1 M KOH solution, whereupon the γ-dichloride went into solution (from which it was later reprecipitated by the addition of HCl), and the $[PtCl_2(NH_3)_2]$ remained in the residue and was analyzed (found %: Pt 64.79; calculated %: Pt 65.04). The molar ratio $[Pt(\gamma H)_2Cl_2]:[PtCl_2(NH_3)_2]$ in the Jörgensen cleavage products was never less than unity. We have noted that, according to our data [1], boiling of the analogous β-alanine derivative with HCl also formed a mixture of $[Pt(\beta H)_2Cl_2]$ and $[PtCl_2(NH_3)_2]$, but with a predominance of $[PtCl_2(NH_3)_2]$. The considerable increase in bond strength on passing from MH to γH, that is from an α-amino acid to the isomeric γ-amino acid was, for us, a surprise. We noted that continued heating of $[Pt(\gamma H)_2(NH_3)_2]Cl_2$ in a drying chamber at 110° did not lead to decomposition of the material. Meanwhile, the analogous compounds with α-alanine and with α-aminobutyric acids turned noticeably yellow (being converted, apparently, into a mixture of $[PtCl_2(NH_3)_2]$ and free amino acid) on short heating at 110°.

It is of interest to compare in detail the behavior of the analogous compounds of Pt^{+2} with α-, β-, γ-, δ-, and ϵ-amino acids. For this purpose, we recently synthesized a compound of Pt^{+2} with ϵ-aminocarproic acid.

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F.E. Dzerzhinsky Dnepropetrovsk
Chemical-Technological Institute

ON THE POSSIBILITY OF PREPARING $Ba(O_2)_2$

I.I. Volnov and A.N. Shatunina

(Presented by Academician I.I. Chernyaev, April 2, 1956)

Among the many representatives of inorganic peroxide compounds, a special place is held by compounds characterized by the presence of the molecule ion O_2^- and known by the name hyperperoxide or superoxide [1,2]. These compounds are colored yellow or brown and are paramagnetic.

The ability to form superoxides is characteristic of the elements of the main sub-group of the first group of the periodic system of D.I. Mendeleev. Superoxides of K, Rb, and Cs are prepared by heating them in an atmosphere of oxygen; sodium superoxide, NaO_2, is prepared by reacting Na_2O_2 with oxygen at a temperature not lower than 200° and a pressure not less than 105 atm. [3].

Up to the present, the corresponding compounds of the alkaline earth metals have not been prepared by this method. Attempts along this line undertaken by Seyb and Kleinberg [4] did not meet with success.

Assuming that the structure of $Ba(O_2)_2$ would be similar to the structure of the known superoxides of the alkali metals, and on the basis of an approximate evaluation of th value of $\log K_{PO_2}$ for the reaction

$$BaO_2\,(s) + O_2\,(g) \rightleftharpoons Ba(O_2)_2\,(s), \qquad (I)$$

the authors of the present paper came to the conclusion that it was possible for the reaction to proceed at superpressures of oxygen and elevated temperatures.

In order to estimate ΔH^0_{298} for Reaction (I), it was necessary to estimate only the heat of formation of $Ba(O_2)_2$, since the heat of formation of BaO_2 is known to be −151.9 kcal [5]. ΔH^0_{298} of $Ba(O_2)_2$ was estimated by us as −166.1 kcal by means of the Born-Haber cycle: $-\Delta H^0_{298}\,Ba(O_2)_2 = -\Delta H^0_{298}\,Ba^{++} + 2E_{O_2^-} + U\,Ba(O_2)_2$, taking $\Delta H^0_{298}\,Ba^{++} = 395.7$ kcal [6], $E_{O_2^-} = 23$ kcal (an average value obtained by means of the same cycle for KO_2 and NaO_2), $U\,Ba(O_2)_2 = 515.8$ kcal (estimated using the formula of A.F. Kapustinsky).

From these data on $\Delta H^0_{298}\,Ba(O_2)_2$ and $\Delta H^0_{298}\,BaO_2$, for Reaction (I), $\Delta H^0_{298} = 151.9 - 166.1 = -14.2$ kcal.

In order to estimate ΔS^0_{298} for Reaction (I) it was necessary to estimate S^0_{298} for $Ba(O_2)_2$ and S^0_{298} for BaO_2. The value $S^0_{298}\,Ba(O_2)_2 = 28.7$ e.u. was estimated graphically from $S^0_{298}\,NaO_2 = 27.7$ e.u. and $S^0_{298}\,KO_2 = 27.9$ e.u. [7] according to $S = A \log M + B$ [8]; $S^0_{298}\,BaO_2$ was estimated from data [5,9] using the equation $\Delta S^0_{298} = -\frac{151.9 + 140}{298} = -39.9$ e.u., whence $S^0_{298}\,BaO_2 = -39.9 + 16$ [6] $+ 49$ [6] $= 25.1$ e.u.

From these data for Reaction (I) $\Delta S^0_{298} = 28.7 - 25.1 - 49 = -45.4$ e.u. Substituting the estimated values in the equation

$$\log K_{PO_2} = -\frac{\Delta H^0_{298}}{4.575\,T} + \frac{\Delta S^0_{298}}{4.575},$$

the authors obtained approximate values for the equilibrium pressure of oxygen in Reaction (I) (see Table 1).

On the basis of these data, a series of experiments was carried out using the apparatus developed by D.S. Tsiklis [10], with which oxygen pressures of 5000 atm. and temperatures up to 500° could be attained; these exper-

TABLE 1

Equilibrium Pressure of Oxygen in the Reaction BaO_2 (s) + O_2 (g) $\rightleftarrows$ $Ba(O_2)_2$ (s)

Temp., °C	25	100	200	210	220	230	250	302
P_{O_2}, atm.	32	75	2300	3150	4230	7278	9750	33600

tments, which were carried out by subjecting BaO_2 to an oxygen pressure of 3300 atm. at 210° for 19 hours, resulted in mixtures of BaO_2 and $Ba(O_2)_2$ containing up to 10.4 wt.% of the latter. The presence of $Ba(O_2)$ was established by analysis for peroxide and superoxide oxygen, the analysis being carried out by the method of Traube [11] using the apparatus proposed by Seyb and Kleinberg [12]. The preparation was heterogeneous. The upper layer was colored, and the lower was white. Apparently, under the conditions under which the experiments were carried out, the reaction proceeds mainly at the boundary between the solid and gas phases.

The experiments were carried out in cooperation with the State Institute for the Nitrogen Industry MKhP USSR under the direction of Prof. L.P. Krichevsky and Doctor of Chemical Science D.S. Tsiklis, to whom the authors express their deep appreciation.

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N.S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences, USSR

THE EFFECT OF THE MICROSTRUCTURE OF POLYISOPRENE ON ITS PROPERTIES

A.A. Korotkov, K.B. Piotrovsky and D.P. Feringer

(Presented by Academician V.A. Kargin, March 24, 1956)

In contrast to radical polymerization, polymers of varying microstructure can be obtained in ionic polymerizations by varying the composition of the catalyst and the reaction conditions; thus, the content of 1,4-isoprene units can be varied from 0 to 94-95% and, therefore, the total of 1,2- and 3,4-isoprene units can be varied from 5-6 to practically 100%.

Polyisoprene prepared by ionic polymerization usually contains only a small amount of 1,2-units, and the ratio of cis- to trans-1,4-units can vary within wide limits. As may be seen from the material presented below, this latter circumstance does not have a substantial effect on the properties which were of interest to us, but it does lead to some scattering of the experimental points. In judging the effect of the degree of regularity of the microstructure on the properties of the polymers, we considered it possible to limit ourselves to a single index – the total content of 1,2- and 3,4-units. This made our problem considerably easier. Infrared spectroscopy in the C–C frequency region (~1000 cm^{-1}), which is used for the separate determination of cis-1,4-, trans-1,4-, 1,2-, and 3,4-isoprene units in the polymer [1-3], is little suited to large-scale testing, and we were able to substitute the more practicable and faster infrared method in the region of the first harmonic of the C–H vibration (~6000 cm^{-1}), which permitted determination of the total 1,2- and 3,4-units with an accuracy of 1-2% [4].

In all (beginning in 1950) we examined more than 250 samples of polyisoprene. Naturally, our chief attention was given to the synthesis of samples with minimum contents of 1,2- and 3,4-monomer units as being samples of the greatest practical interest, since they approach natural rubber in properties.

As would be expected, high strength in unreinforced rubber recipes (5 phr magnesium oxide, 2.5 phr* stearic acid, 1.5 phr diphenylguanidine, and 3 phr sulfur; 40-80 minutes vulcanization time at 142°) was exhibited by those polymers with a minimum content of 1,2- and 3,4-units, i.e., by polymers with the most regular structure, in which self-reinforcement of the rubber was possible by virtue of crystallization or high orientation of the polymer chains during stretching [5]. At contents of 1,2- and 3,4-units of 5-7% the rubbers approached natural rubber vulcanizates in strength (220-240 kg/sq. cm. for the recipe given, and reaching 300 kg/sq. cm. and higher in other recipes).

Polymers containing from 15 to 65% 1,2- and 3,4-units did not differ in strength from ordinary synthetic rubbers of irregular microstructure (20-50 kg/sq. cm.). With a further increase in the content of 1,2- and 3,4-units in the polymer, the rubber again exhibited self-reinforcement during stretching as a result of the greater regularity of the microstructure owing to the predominance of 3,4-isoprene units in the polymer (see Figure 1). However, such a polymer possesses little elasticity; the elasticity as indicated by recovery at room temperature leveled out at 5% (see Figure 3), and the relative elongation decreased sharply (see Figure 2). Polymers with a low content of 1,2- and 3,4-units had an appreciably higher elongation at break than natural rubber vulcanizates (see Figure 2). This is explained by the appearance of the phenomenon of chain orientation at higher strain for those polymers with less regular structure than natural rubber.

The vitrification temperature of isoprene polymers increases almost linearly with an increase in content of 1,2- and 3,4-units (see Figure 4). At contents close to 100%, the polymer, both in the vulcanized and in the unvulcanized state, is strongly crystallized and is not elastic.

*Parts per hundred – Translator.

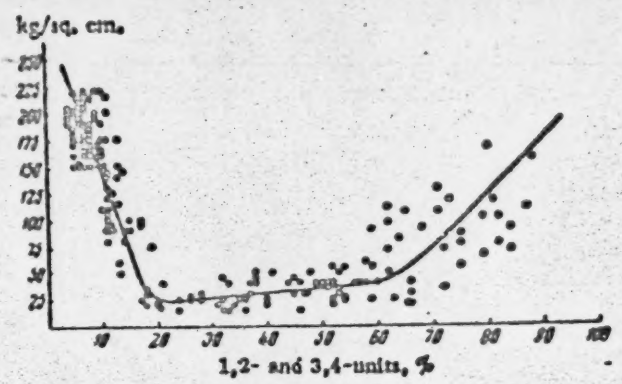


Fig. 1.

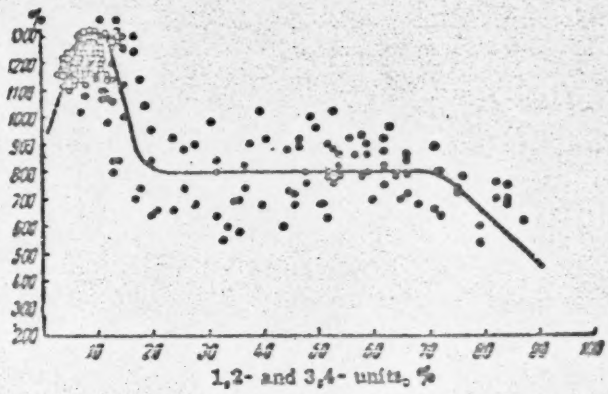
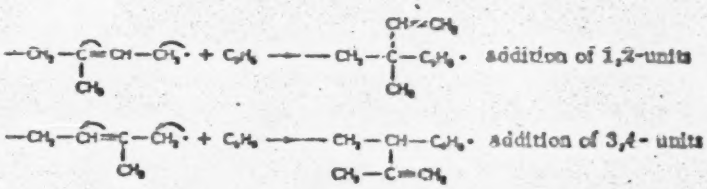


Fig. 2.

By bulk or emulsion polymerization of isoprene by a radical mechanism, polymers can be obtained containing approximately equal amounts of 1,2- and 3,4-units, the total of which is 5-7% and 90-95% 1,4-units, chiefly in trans-configuration [3,6]. Such polymers approach gutta-percha in their properties, and the unreinforced rubbers have relatively high strength characteristics. Meanwhile, they behave as synthetic rubbers of irregular structure. This phenomenon can be explained by the following example.

During radical polymerization, attachment of the isoprene units to the polymer chain proceeds by the addition of a molecule of monomer to the end of the growing polymer chain. Consequently, the presence of 1,2- and 3,4-units in the polymer is the result of the addition of the monomer molecules to two forms of radicals:



Since the contents of 1,2- and 3,4-units in the polymers are approximately equal [3,6], both forms of terminal groups in the growing polymer chains are present in equal amounts; in other words, the successive addition of isoprene molecules by either the first or fourth atom is equally probable during polymerization. Therefore, we can conclude that 1,4-units of isoprene in polymers obtained by radical polymerization are added both 1,4 and 4,1 with equal probability according to statistical distribution. Thus, heterogeneity exists in similar polymers with respect to "head-to-tail" and "head-to-head" addition of the monomer units, which leads to irregular microstructure.

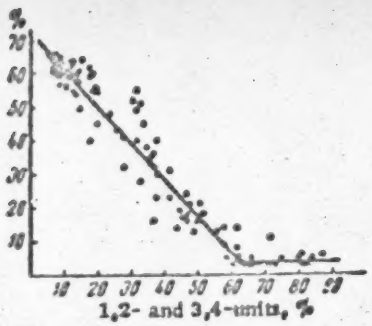


Fig. 3.

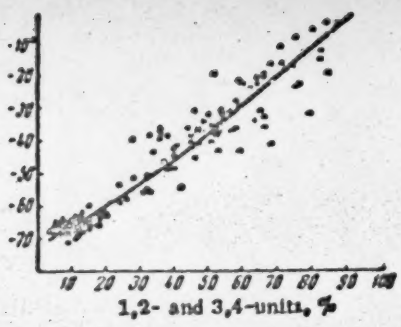
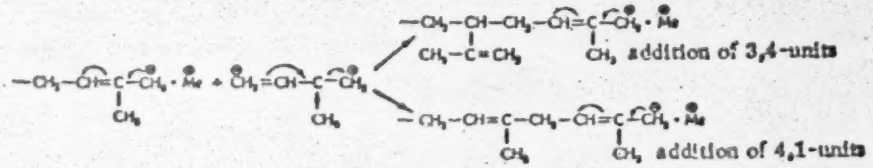


Fig. 4.

In ionic polymerization, the active center is a dipole of complex structure. During the polymerization of isoprene, the small shifting of charges in the monomer molecules as a result of the inductive effect of the methyl group is sufficient for oriented addition of the isoprene molecule chiefly through the fourth carbon atoms



Therefore, in isoprene polymers prepared by ionic polymerization heterogeneity with respect to "head-to-tail" and "head-to-head" addition is not essentially significant, and, with a low content of 1,2- and 3,4-units, they approach natural rubber in their properties.

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S.V. Lebedev All-Union Research Institute
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DEHYDROCHLORINATION OF DICHLOROISOPROPYLTRICHLOROSILANES AND METHYLATION OF CHLOROISOPROPENYLTRICHLOROSILANES

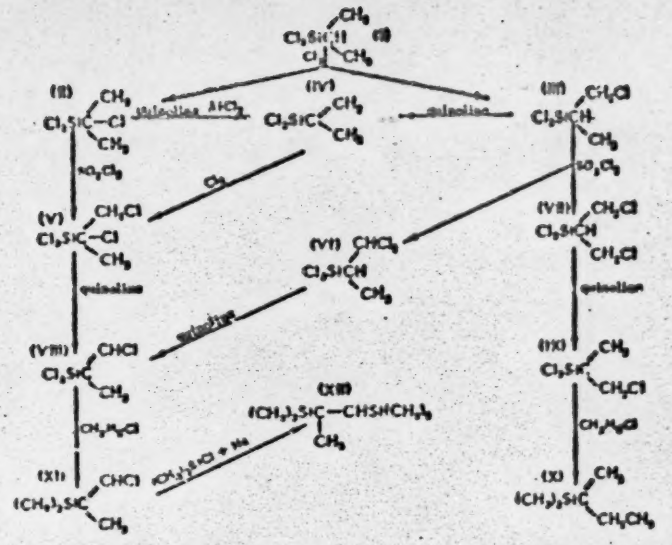
Associate Member of the Academy of Sciences A.D. Petrov, V.F. Mironov and V.G. Glukhovtsev

In previous papers [1,2] we reported that, in contrast to β-chloroethyltrichlorosilane which undergoes so-called β-cleavage during methylation,

$$Cl_3SiCH_2CH_2Cl + 4CH_3MgX \rightarrow (CH_3)_4Si + CH_2=CH_2,$$

β-chlorovinyltrichlorosilane methylates without β-cleavage. It was also found that 1,2-bis(trimethylsilyl)ethylene, $(CH_3)_3SiCH=CHSi(CH_3)_3$, is characterized by an unusually high exaltation of its molar refraction and by a very broad and intense line at its Raman spectra at the frequency characteristic of a double bond. These phenomena were explained by σ–σ-conjugation of the Si–C bond with C–Cl or Si–C bonds separated by a multiple bond. In the light of this, we planned a route for the synthesis of close homologs of the above-mentioned compounds.

Isopropyltrichlorosilane (I) has been chlorinated previously [4] only with sulfuryl chloride, yielding α- and β-chloroisopropylsilane (II) and (III) in a ratio of 1:3 and in a yield of 33%. By photochemical chlorination of $i\text{-}C_3H_7SiCl_3$, which we carried out under previously described conditions [5], the α- and β-isomers (II) and (III) were obtained in a ratio of 1:1.7 and a yield of 92%. Further chlorination of α-chloroisopropyltrichlorosilane (II) with sulfuryl chloride led to the only possible dichloride, α,β-dichloroisopropyltrichlorosilane (V) with a b.p. of 23-27° (see Scheme 1). Chlorination of β-chloroisopropyltrichlorosilane under these same conditions would be expected to lead to the three dichlorides (V), (VI), and (VII). However, (V) was apparently not formed, since we isolated only two substances, and both froze below –60°. However, the presence of (V) in (VI) in the form of a minor impurity is not excluded. Dehydrochlorination by quinoline of the three dichlorides (V), (VI), and (VII) led to the formation of the two theoretically possible forms of chloroisopropenyltrichlorosilane (VIII) and (IX). The structures of compounds (V), (VI), (VII), (VIII), and (IX) were demonstrated both by their method of preparation and by subsequent transformations (see Scheme 1). Methylation of 2-trichlorosilyl-1-chloro-1-propene (VIII) and 2-trichlorosilyl-3-chloro-1-propene (IX) proceeded without any β-cleavage. Especially interesting results were obtained in the latter case where the polar Si–C and C–Cl bonds are separated by a single, not a multiple, bond, i.e., just as in $Cl_3SiCH_2CH_2Cl$; however, β-cleavage did not occur here apparently because of the presence in the molecule of a multiple bond and σ–π-conjugation of it with the C–Cl bond. Moreover, this circumstance is also dependent on the especially high activity of the chlorine in the β-position, which is easily substituted by a methyl radical. Condensation of α-methyl-β-chlorovinyltrimethylsilane (XI) with trimethylchlorosilane in the presence of sodium gave 1,2-bis(trimethylsilyl)methylethylene (XII). This closest homolog of the previously synthesized 1,2-bis(trimethylsilyl)-ethylene [1,2] also exhibited considerable exaltation.



The dehydrochlorination of compounds (II) and (III) with aluminum chloride also gave interesting results. The β-chloride (III) formed only a heavy oil (apparently the product of polymerization of isopropenyltrichlorosilane) even when the process was carried out in a vacuum. Upon distillation with a catalytic amount of $AlCl_3$, the α-chloride (II) is converted to (IV) in 44.5% yield, but α-chloroethyltrichlorosilane under analogous conditions formed vinyltrichlorosilane in an overall yield of only 15%. It was further shown that the α-chloride (II) is dehydrochlorinated with a 21.5% yield even by quinoline, while α-chloroethyltrichlorosilane when acted upon by quinoline forms vinyltrichlorosilane with an overall yield of only 10%. All this attests to the greater tendency toward cleavage possessed by the chlorine attached to a tertiary α-carbon in comparison with a secondary α-carbon. By adding chlorine to (IV) we obtained the dichloride (V) which had properties identical with those of the dichloride obtained by chlorination of compound (II). However, the freezing points of these dichlorides (V) obtained by these different routes differed by ~10°, probably owing to a small amount of impurities. It should also be noted that the substances prepared by dehydrochlorination of (V) and (VI) differed somewhat with respect to n_D^{23}, but had completely identical Raman spectra (determined by Yu.P. Egorov). In Table 1 are presented the physical properties and analyses of the compounds synthesized (compounds marked with an asterisk were prepared for the first time).

EXPERIMENTAL

Isopropyltrichlorosilane $Cl_3SiCH(CH_3)_2$ (I). 1-C_3H_7MgBr, prepared from 146 g Mg and 780 g isopropyl bromide in 1.5 liters of ether, was added with cooling and vigorous stirring to 1550 g of $SiCl_4$ in 0.5 liter of ether in a 4-liter flask. On the following day, after boiling for 1.5 hours, the contents of the flask were filtered from the magnesium salt and washed twice with fresh ether. Distillation in a column gave 536 g of (I); b.p. 119-120°. α-Chloroisopropyltrichlorosilane $Cl_3SiCCl(CH_3)_2$ (II). β-Chloroisopropyltrichlorosilane $Cl_3SiCHCH_2(CH_2Cl)$ (III). 1051 g of (I) was placed in the flask of the apparatus [5]. Chlorination was carried out at a temperature in the flask of 148° and required 63 hours. Distillation of the 1170 g of product gave 230 g of the original (I), 340 g of (II), b.p. 151°, and 560 g of (III), b.p. 164°. There was 33 g of kettle residue.

Isopropyltrichlorosilane $Cl_3SiC(CH_3)=CH_2$ (IV). A. A mixture of 74 g of (II) and 64 g of quinoline was distilled at the usual rate from a flask at a temperature of 220°. Distillation of the distillate in a column gave 13 g (IV), b.p. 115-116°, and 21 g of the original (II).

B. 73 g of (II) was distilled at the usual rate from a flask in the presence of 1 g of $AlCl_3$. Distillation of the distillate in a column gave 27 g of (IV), b.p. 116°, and 6 g of the original (II).

α,β-Dichloroisopropyltrichlorosilane $Cl_3SiCCl(CH_3)CH_2Cl$ (V). A. A mixture of 230 g of α-chloride (II), 155 g of SO_2Cl_2, and 0.5 g of benzoyl peroxide was heated for 10 hours until the evolution of gas ceased. 0.5 g

TABLE 1

Compound	B.p., °C	Press mm Hg	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Yield, %	Found % C	Found % H	Found % Si	Found % Cl	Calculated % C	Calculated % H	Calculated % Si	Calculated % Cl
I $Cl_2SiCH(CH_3)_2$	119	745	1.4335	1.2024	38.39	38.43	51	—	—	—	—	—	—	—	—
II $Cl_2SiCH_2(CH_3)_2$	131	744	—	—	—	—	92	—	—	—	—	—	—	—	—
III $Cl_2SiCH(CH_3)CH_2Cl$	164	744	1.4670	1.3520	43.42	43.27		—	—	—	—	—	—	—	—
IV $Cl_2SiC(=CH_2)CH_3$	119.5	731	1.4450	1.2285	37.99	37.98		—	—	—	—	—	—	—	—
VA* $Cl_2SiCH(CH_3)CH_2Cl$	186.5	740	—	—	—	—	61	14.96 14.96	2.22 2.01	11.31 11.22	70.92 70.80	14.62	2.04	11.39	71.93
VB* ditto	191	752	1.4870	1.4711	48.18	48.11	91.5	—	—	—	—	—	—	—	—
VI* $Cl_2SiCH(CH_3)CHCl_2$	192.5	754	1.4862	1.4760	47.98	48.11	85.5	14.74 14.72	1.98 2.10	11.62 11.59	71.46 71.50	14.62	2.04	11.39	71.93
VII* $Cl_2SiCH(CH_2Cl)_2$	205	754	1.4940	1.4947	48.00	48.11		14.75 14.67	2.06 2.02	11.31 11.30	71.58 71.76	14.62	2.02	11.39	71.93
VIIIA* $Cl_2SiC(=CH_2)CH_3$	154	737	1.4815	1.3830	43.24	42.90	36	16.35 16.12	1.56 1.77	13.31 13.37	68.03 68.17	17.16	1.92	13.37	67.54
VIIIB* ditto	153	743	1.4780	1.3820	43.00	42.90	22	—	—	—	—	—	—	—	—
IX* $Cl_2SiCCH_2Cl(=CH_2)$	164	750	1.4794	1.3967	42.65	43.00	36.5	17.05 17.15	1.85 1.90	13.30 13.31	67.80 67.60	17.16	1.92	13.37	67.54
X* $(CH_3)_2SiCCH_2CH_2$	110	771	1.4165	0.7682	43.28	43.20	45.5	65.60 65.70	12.85 12.70	21.50 21.35	—	65.53	12.57	21.89	—
XI* $(CH_3)_2SiC(=CH_2)CHCl$	137.5	752	1.4500	0.9045	44.18	43.91	65	48.56 48.69	8.75 8.84	19.04 18.85	23.30 23.75	48.45	8.81	18.98	23.86
XII* $(C_2H_5)_2SiC(=CH_2)CHSi(CH_3)_3$	183.5	750	1.4435	0.7809	63.36	62.50	68	58.19 58.10	12.00 12.10	29.60 29.80	—	57.97	11.59	30.13	—

portions of benzoyl peroxide were added twice during the course of the reaction. Distillation in a column gave 10 ml of SO_2Cl_2, 100 g of the original α-chloride (II), and 92 g of the dichloride (V), b.p. 188.5°, n_D^{20} 1.4845, m.p. 23 to 27°. There were also 31 g of higher boiling liquid and 10 g of kettle residue.

C. Chlorine was passed for 20 hours through 59 g of (IV). A sharp evolution of heat occurred periodically. Distillation, after obtaining the theoretical weight increase, gave 76 g of the dichloride (V), b.p. 191° (752 mm). n_D^{20} 1.4840. However, it melted at −7 to +13°, due, probably, to a small amount of impurities.

1,1-Dichloro-2-(trichlorosilyl)propane $Cl_3SiCH(CH_3)CHCl_2$ (VI). 1,2-dichloro-2-(trichlorosilyl)propane $Cl_3SiCH(CH_2Cl)_2$ (VII). A mixture of 303 g of the β-chloride (III), 230 g of SO_2Cl_2, and 0.5 g of benzoyl peroxide was heated for 8 hours. 0.5 g portions of benzoyl peroxide were added twice when gas formation abated. Distillation in a column gave 67.6 g of the original (III), 116 g of the dichloride (VI), b.p. 192.5°, and 117 g of the dichloride (VII), b.p. 205°. The kettle residue consisted of 20 g of tar. The dichloride (VI) did not crystallize on being cooled to −50°.

α-Methyl-β-chlorovinyltrichlorosilane $Cl_3SiC(CH_3)=CHCl$ (VIII). A. A mixture of 80 g of dichloride (V) and 50 g of quinoline was slowly distilled from a flask. The distillate was filtered from the salt floc and distilled in a column. 18 ml of $SiCl_4$ and 24 g of compound (VIII), b.p. 154-154.5°, were obtained.

B. 8 ml of $SiCl_4$ and 24 g of compound (VIII), b.p. 153°, were obtained in a similar manner from 116 g of dichloride (VI) and 73 g of quinoline. The yield was 29.5%. Raman spectra of this compound were in complete agreement with the spectra of compound (VIII) obtained in synthesis A.

3-Chloro-2-(trichlorosilyl)-1-propene $Cl_3SiC(CH_2Cl)=CH_2$ (IX). 36 g of (IX), b.p. 164°, was obtained by a similar method from 117 g of dichloride (VII) and 73 g of quinoline.

α-Ethylvinyltrimethylsilane $(CH_3)_3SiC(CH_2CH_3)=CH_2$ (X). To CH_3MgCl, prepared from 15 g of Mg in 0.25 liter of ether, was added 35 g of (IX). On the following day, the contents of the flask were boiled 3 hours and then decomposed with water. After drying with $CaCl_2$, the ether layer was distilled in a column to yield 9.8 g of (X), b.p. 110°.

α-Methyl-β-chlorovinyltrimethylsilane $(CH_3)_3SiC(CH_3)=CHCl$ (XI). 51 g of (VIII) was added to CH_3MgCl prepared from 23 g of Mg in 0.5 liter of ether. After the usual treatment, 23.4 g of (XI) was obtained, b.p. 137.5°.

1,2-bis(trimethylsilyl)methylethylene $(CH_3)_3SiC(CH_3)=CHSi(CH_3)_3$ (XII). 10 g of Na was melted in 60 ml of boiling toluene and broken up into a fine dispersion by a high-speed stirrer. After cooling, the toluene was decanted and replaced by 200 ml of ether. 20 g of $(CH_3)_3SiCl$, 1 ml of ethyl acetate, and ~5 ml of (XI) were added to the flask. After initiation of the reaction, 22 g of (XI) was added. After boiling for 5 hours, the contents of the flask were filtered from the salt, which was washed with fresh ether. Distillation in a column gave 16.5 g of the disilane (XII), b.p. 163.5° (759 mm).

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N.D. Zelinsky Institute of Organic Chemistry
Academy of Sciences, USSR

* T.p. = C.B. Translation pagination.

SOME DERIVATIVES OF DISILANEPROPANE

Academician A.V. Topchiev, N.S. Nametkin, T.I. Chernysheva and S.G. Durgaryin

In 1947, a new method was reported for the preparation of organosilicon compounds containing a carbon bridge between two silicon atoms [1]. Hexachlorodisilaneethane and hexachlorodisilanepropane were prepared by the authors according to the following scheme:

$$Cl_3SiCH = CH_2 + HSiCl_3 \rightarrow Cl_3SiCH_2CH_2SiCl_3,$$

$$Cl_3SiCH_2CH = CH_2 + HSiCl_3 \rightarrow Cl_3SiCH_2CH_2CH_2SiCl_3.$$

In 1953, an investigation [2] was published in which was described the preparation of organosilicon compounds by the reaction of alkylvinylsilanes and alkylarylvinylsilanes with trichlorosilane in the presence of acetyl peroxide:

$$R_2SiCH = CH_2 + HSiCl_3 \rightarrow R_2SiCH_2CH_2SiCl_3$$

$$R_2Si\begin{matrix}CH = CH_2\\ CH = CH_2\end{matrix} + 2HSiCl_3 \rightarrow R_2Si\begin{matrix}CH_2CH_2SiCl_3\\ CH_2CH_2SiCl_3\end{matrix}$$

It appeared to us to be of interest to study the reactions of different allylsilanes with silicon compounds containing an Si–H bond. The syntheses were carried out according to:

$$A_3SiCH_2CH = CH_2 + HSiB_3 \rightarrow A_3SiCH_2CH_2CH_2SiB_3,$$

where A is CH_3, C_2H_5, C_4H_9, C_6H_5, or Cl; B is Cl or C_6H_5.

The investigation showed that the activity of the double bond in allylsilanes toward addition reactions depends on the nature of the substituent atoms and groups bonded to the silicon. Thus, there was practically no reaction when it was attempted to react trimethylallylsilane and triethylallylsilane with trichlorosilane in the presence of benzoyl peroxide at 50°. Under the same conditions with tributylallylsilane, the yield of addition product was 13%. Products of the addition of trichlorosilane to trimethylallylsilane and triethylallylsilane were prepared only in an autoclave at a temperature of 100-120°; however, in this case the yields were very small, 2.5 and 10%, respectively.

These data indicate that the activity of the double bond in the allyl group increases with an increase in the size of the organic radicals in the trialkylallylsilanes. Upon substitution of the alkyl radicals in trialkylallylsilanes by substituents having an electronegative character (phenyl radical or chlorine), the double bond in the allyl radical becomes still more active. Thus, the reaction of trichlorosilane with phenyldimethylallylsilane gave phenyldimethyltrichlorodisilanepropane in 22% yield, and the reaction with trichloroallylsilane gave hexachlorodisilanepropane in 62% yield.

Similar results were obtained in reactions of allyl derivatives of silicon with triphenylsilane. Trimethyltriphenyldisilane propane was obtained in 2.8% yield by the reaction of triphenylsilane with trimethylallylsilane, and hexaphenyldisilanepropane was obtained in 36% yield from triphenylallylsilane.

Compound	Formula	B.p., °C	Pressure, mm Hg	M.p., °C	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.	Cl, % found	Cl, % calc.
Trichlorotrimethyldisilanepropane	$(CH_3)_3SiC_3H_6SiCl_3$	93—94	10	—	1.1016	1.4511	61.65	61.98	42.93 42.76	42.42
Trichlorotriethyldisilanepropane	$(C_2H_5)_3SiC_3H_6SiCl_3$	98—100	5	—	1.0659	1.4673	75.81	75.84	35.20 35.81	36.43
Trichlorotributyldisilanepropane	$(C_4H_9)_3SiC_3H_6SiCl_3$	189—191	7	—	1.0160	1.4803	104.03	103.62	27.21 27.20	27.30
Phenyldimethyltrichlorodisilanepropane	$C_6H_5(CH_3)_2SiC_3H_6SiCl_3$	173—175	7	—	1.1415	1.5117	81.81	82.58	33.85 33.79	34.08
Hexachlorodisilanepropane	$Cl_3SiC_3H_6SiCl_3$	115—117	4	29—30	--	—	—	—	67.37 67.20	68.48

Compound	Formula	B.p., °C	Pressure mm Hg	M.p., °C	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.	Found C	Found H	Calc. C	Calc. H
Hexamethyldisilanepropane	$(CH_3)_3SiC_3H_6Si(CH_3)_3$	184—186	748	—	0.7568	1.4231	63.30	63.06	57.30 57.25	12.25 12.30	57.37	12.74
Hexaethyldisilanepropane	$(C_2H_5)_3SiC_3H_6Si(C_2H_5)_3$	112—113	5	—	0.8241	1.4628	90.87	90.84	65.91 65.88	13.10 13.31	66.09	13.31
Hexabutyldisilanepropane	$(C_4H_9)_3SiC_3H_6Si(C_4H_9)_3$	210—212	5	—	0.8400	1.4680	145.83	146.20	73.46 73.46	13.49 13.51	73.55	13.72
Hexaphenyldisilanepropane	$(C_6H_5)_3SiC_3H_6Si(C_6H_5)_3$	—	206.5—210	—	—	—	—	—	83.08 83.29	6.47 6.48	83.52	6.47
Trimethyltriphenyldisilanepropane	$(CH_3)_3SiC_3H_6Si(C_6H_5)_3$	—	173—175	-	—	—	—	—	76.88 76.86	8.01 7.89	76.94	8.07

A series of hexaalkyl derivatives of distilanepropane was obtained by the reaction of chloro derivatives of distilanepropane with lithium alkyls.

EXPERIMENTAL

The allyl derivatives of silicon were prepared by the reaction of allylmagnesium bromide with silicon tetrachloride or trialkylchlorosilanes. The properties of trichloro[illegible], trimethylallylsilane, triethylallylsilane, and tributylallylsilane agreed with the literature values [3]. The properties of phenyldimethylallylsilane and triphenylallylsilane differed somewhat from those given in the literature [4,5].

Phenyldimethylallylsilane. 38 g (61.7% yield) of phenyldimethylallylsilane was prepared from 60 g of phenyldimethylchlorosilane, 24 g of magnesium, and 121 g of allyl bromide: b.p. 70° at 4 mm; d_4^{20} 0.8915; n_D^{20} 1.5069; found MR_D 58.4; calculated for $C_{11}H_{16}Si$ 58.74.

Found %: C 75.05; 74.80; H 9.16; 9.14. $C_{11}H_{16}Si$. Calculated %: C 74.96; H 9.15.

Triphenylallylsilane. From 57 g of triphenylchlorosilane, 20 g of magnesium, and 100 g of allyl bromide was obtained 23.5 g (40.7% yield) of triphenylallylsilane: b.p. 190° at 5 mm; m.p. 90-91°.

Found %: C 83.41; 83.58; H 6.54; 6.43. $C_{21}H_{20}Si$. Calculated %: C 83.95; H 6.70.

Hexachlorodisilanepropane. A mixture of 10 g of allyltrichlorosilane, 20 g of trichlorosilane, and 0.5 g of benzoyl peroxide was heated for 18 hours at a temperature of 40-60°. 11.2 g was obtained; yield 62.2%.

Trimethyltrichlorodisilanepropane. A mixture of 65 g of trimethylallylsilane, 487 g of trichlorosilane, and 5 g of benzoyl peroxide was heated for 18 hours in an autoclave at a temperature of 100-120° and a pressure of 300 atm. 2.0 g was obtained; yield 2.5%.

Triethyltrichlorodisilanepropane. A mixture of 92 g of triethylallylsilane, 540 g of trichlorosilane, and 10 g of benzoyl peroxide was heated for 12 hours in an autoclave at 100-120°. 7 g was obtained; yield 10%.

Tributyltrichlorodisilanepropane. A mixture of 47 g of tributylallylsilane, 82 g of trichlorosilane, and 5 g of benzoyl peroxide was heated in a flask at a temperature of 40-60° for 18 hours. 10 g was obtained; yield 13.2%.

Phenyldimethyltrichlorodisilanepropane. A mixture of 35 g of dimethylphenylallylsilane, 55 g of trichlorosilane, and 4 g of benzoyl peroxide was heated for 16 hours at a temperature of 40-60°. 13.6 g was obtained; yield 22%.

Hexamethyldisilanepropane. 18 g of hexachlorodisilanepropane was added to methyllithium prepared from 15 g of lithium and 183 g of methyl iodide in 400 ml of ether. The reaction mixture was heated for 8 hours on a boiling water bath. 9.2 g was obtained; yield 85%.

Hexaethyldisilanepropane. 16 g of triethyltrichlorodisilanepropane was added to ethyllithium prepared from 7 g of lithium and 54 g of ethyl bromide in 200 ml of ether. The reaction mixture was heated for 10 hours on a boiling water bath. 12 g was obtained; yield 81%.

Hexabutyldisilanepropane. 14 g of tributyltrichlorodisilanepropane was added to butyllithium prepared from 9 g of lithium and 95 g of butyl bromide in 300 ml of ether. The reaction mixture was heated for 6 hours. 10 g was obtained; yield 60.9%.

Hexaphenyldisilanepropane. A mixture of 10 g of triphenylallylsilane, 25 g of triphenylsilane (m.p. 43°), and 1 g of benzoyl peroxide in 100 ml of normal heptane was heated for 10 hours at 100°. 6.8 g was obtained; yield 36.4%.

Trimethyltriphenyldisilanepropane. A mixture of 20.5 g of trimethylallylsilane, 44.8 g of triphenylsilane, and 3 g of benzoyl peroxide in 200 ml of normal heptane was heated for 28 hours at 60° and 10 hours at 100°. 1.8 g was obtained; yield 2.8%.

The analyses for halide were carried out by L.I. Kazelova.

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Institute of Petroleum, Academy of Sciences, USSR

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SYNTHESIS OF ACID CHLORIDES OF THIOPHOSPHINIC* ACIDS [$RPSCl_2$ and R_2PSCl]

Associate Member of the Academy of Sciences M.I. Kabachnik and N.N. Godovikov

Up to the present, acid chlorides of thiophosphinic acids [thiophosphorus acids] have been difficultly available. A basic method for their synthesis has been the addition of sulfur to a chlorophosphine:

$$RPCl_2 + S \rightarrow RPSCl_2.$$

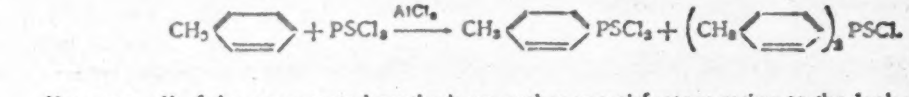
The sulfur donors usually used are elemental sulfur [1], $PSCl_3$ [2], S_2Cl_2 [3], and P_2S_5 [4]. This reaction is sometimes carried out in the presence of a catalyst, such as $AlCl_3$, $FeCl_3$, $ZnCl_2$, or BF_3 [4]. The preparation of ethylthiophosphonyl chloride by the action of hydrogen sulfide on a complex of phosphorus trichloride with ethyl chloride and $AlCl_3$ has been described [5]:

$$[C_2H_5PCl_3]^+ [AlCl_4]^- + H_2S \rightarrow [HAlCl_4 + C_2H_5PCl_2SH] \rightarrow C_2H_5PSCl_2.$$

We may also mention the synthesis of β-alkoxyvinylthiophosphonyl chlorides by the action of hydrogen sulfide on the addition product of phosphorus pentachloride and a vinyl ether [6]:

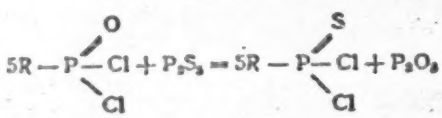
$$ROCHCl - CH_2PCl_4 \cdot PCl_5 + 2H_2S \rightarrow ROCH = CHPSCl_2 + PSCl_3 + 5HCl.$$

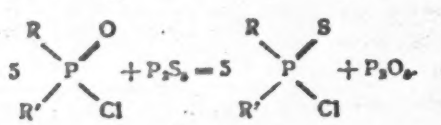
In addition, the preparation of acid chlorides of thiophosphinic acids [thiophosphorus acids] by a Friedel-Crafts-type reaction, for example, from toluene and $PSCl_3$, has been described [7]:



However, all of the enumerated methods are rather unsatisfactory owing to the lack of availability of the initial chlorophosphines or to the low yields of acid chlorides of thiophosphinic acids [thiophosphorus acids].

In the present paper, a method is described for the preparation of acid chlorides of thiophosphinic [thiophosphorus] acids from the acid chlorides of the phosphinic [phosphorus] acids $RPOCl_2$ or R_2POCl, which are comparatively more available compounds than the chlorophosphines. We found that the substitution of sulfur for oxygen with the formation of the acid halides of the thio acids proceeds smoothly by the action of phosphorus pentasulfide on the acid chlorides of the phosphinic [phosphorus] acids in the temperature interval 135-160°:





* Translators note: "Thiophosphinic" is term used by the authors, apparently as generic for both thiophosphinic and thiophosphonic.

We synthesized by this method methyl-, chloromethyl-, ethyl-, propyl-, cyclohexyl- and phenylphosphonyl chlorides and also methyl-cyclohexylphosphinyl chloride with yields of 53 to 85% of theoretical. All of the acid chlorides prepared were characterized by conversion to the corresponding mono- or dianilides. The constants of these substances are presented in Table 1.

TABLE 1

Formula	B.p., °C	Pressure, mm Hg	M.p., °C	n_D^{20}	d_4^{20}	Yield, %	Analysis, % C found	C calc.	H found	H calc.	P found	P calc.	N found	N calc.
CH_3PSCl_2	34—35	8	—	1.5520	1.4302	85	8.1 7.9	8.1	2.0 2.1	2.0	—	—	—	—
$CH_3PS(NHC_6H_5)_2$	—		177—178	—	—	quant.	59.3 59.2	59.5	5.7 5.7	5.8	12.0 11.8	11.8	12.4 11.5	12.3
$ClCH_2PSCl_2$	58—59	8	—	1.5770	1.5094	80	6.5 6.3	6.5	1.2 1.1	1.1	—	—	—	—
$ClCH_2PS(NHC_6H_5)_2$	—		118—118.5	—	—	quant.	52.4 52.5	52.6	4.8 4.7	4.8	—	—	—	—
$C_2H_5PSCl_2$*	50—51	8	—	1.5450	1.3643	71	—	—	—	—	—	—	—	—
$C_2H_5PS(NHC_6H_5)_2$**	—		112—114	—	—	quant.	60.4 60.5	60.8	6.5 6.4	6.2	10.9 11.1	11.2	11.3 11.2	11.6
$C_3H_7PSCl_2$***	88—87	10	—	1.5360	1.3005	83	—	—	—	—	—	—	—	—
$C_3H_7PS(NHC_6H_5)_2$	—		139	—	—	quant.	62.1 62.0	62.0	6.7 6.7	6.6	10.8 11.0	10.7	11.0 11.1	11.0
$C_6H_{11}PSCl_2$	76—77	2	—	1.5022	1.2037	71	33.4 33.5	33.2	4.9 5.0	5.1	—	—	—	—
$C_6H_{11}PS(NHC_6H_5)_2$	—		122—123	—	—	quant.	64.5 65.3	65.4	6.9 7.0	7.0	9.3 9.2	9.4	9.4 9.4	9.5
$CH_3(C_6H_{10})PSCl$	89—90	2	—	1.5570	1.1713	70	42.6 42.6	42.7	7.3 7.2	7.2	—	—	—	—
$CH_3(C_6H_{10})PSNHC_6H_5$	—		135.5—136	—	—	quant.	61.6 61.8	61.6	6.1 6.1	6.0	—	—	—	—
$C_6H_5PSCl_2$****	87—88	3	—	1.6250	1.4042	65	34.0 34.1	34.1	2.6 2.6	2.4	—	—	—	—
$C_6H_5PS(NHC_6H_5)_2$	—		175—176	—	—	quant.	66.2 66.2	66.6	5.2 5.0	5.3	9.3 9.3	9.5	9.3 9.3	9.3

*From [17]: b.p. 88.5-89°/46 mm; n_D^{20} 1.5440; d_4^{20} 1.3550.
**From [5]: m.p. 112-114°.
***From [1]: b.p. 88-90°/50 mm; d^{20} 1.3018.
****From [2]: b.p. 150°/26 mm [2]; d^{18} 1.376 [18].

In the calculation of the molecular refractions of these acid chlorides, we at first used 4.27 as the value of the atomic refractivity of phosphorus in alkylphosphinic acids [8], 4.85 as the atomic refractivity of phosphorus in dialkylphosphinic acids [9], 9.70 for sulfur [10], and 6.336 for chlorine in acid chlorides [8]. Using these values, exaltation of the molecular refraction was relatively constant and averaged 0.83, as may be seen from the data of Table 2.

TABLE 2

Formula	Found MR_D	Calc. with $AR_S = 9.70$: MR_D	ΔMR_D	Calc. with $AR_S = 10.53$: MR_D	ΔMR_D
CH_3PSCl_2	33.29	32.36	0.93	33.19	+0.10
$ClCH_2PSCl_2$	34.05	37.23	0.80	34.06	—0.04
$C_2H_5PSCl_2$	37.74	36.94	0.80	37.82	—0.07
$C_3H_7PSCl_2$	42.45	41.60	0.85	42.43	+0.02
$C_6H_{11}PSCl_2$	54.02	53.25	0.77	54.08	—0.06
$CH_3(C_6H_{10})PSCl$	54.08	53.21	0.85	54.04	+0.02
Average			+0.83		±0.05

Considering the ease with which the atomic refractivity of sulfur is affected by constitutive effects, we assumed that in acid chlorides of thiophosphinic [thiophosphorus] acids the atomic refractivity of sulfur should be taken, not as 9.70, but as 9.70 + 0.83, i.e., 10.53. With this change, as may be seen from the data of Table 2 (last two columns), good agreement was obtained between the found and calculated molecular refractions.

Methyl- [11], chloromethyl- [12], ethyl- [13], propyl-, cyclohexyl- [14], and phenyl- [15] phosphonyl chlorides and methylcyclohexylphosphinyl chloride [16] were used as the starting materials for the syntheses of the acid chlorides of thiophosphinic (thiophosphorus)

acids*.

The propylphosphonyl chloride was prepared by heating the diethyl ester of propylphosphonic acid with phosphorus pentachloride at 130-160° for 2 hours with simultaneous distillation of the phosphoryl chloride formed. The yield was 90%; b.p. 63-64.5°/10 mm; n_D^{20} 1.4630; d_4^{20} 1.3148. Literature data: b.p. 88-90°/50 mm; d^{20} 1.3088.

Acid chlorides of thiophosphinic (thiophosphorous) acids. A mixture of 0.1 mole of the acid chloride of the phosphinic [phosphorous] acid and 0.025 mole of P_2S_5 was heated at 135-160° in an atmosphere of CO_2 for 3-4 hours, after which the liquid was distilled, washed with cold water, dried over calcined sodium sulfate, and distilled under vacuum. The yields, constants, and analytical data on the acid chlorides prepared and of their anilides are presented in Table 1.

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THE SIMULTANEOUS DETERMINATION OF OXYGEN AND HALIDES (CHLORINE, BROMINE, AND IODINE) IN ORGANIC COMPOUNDS

M.O. Korshun and E.A. Bondarevskaya

(Presented by Academician A.N. Nesmeyanov, April 18, 1956)

In the course of an investigation of a method for the direct determination of oxygen based on the method of M.O. Korshun [1-4], we found the direct simultaneous determination of oxygen and halide to be possible.

As is well known, the essence of the direct determination of oxygen is thermal decomposition of the material in a stream of nitrogen, conversion of all the oxygen to CO over incandescent carbon, further oxidation of the CO to CO_2, and gravimetric or volumetric determination of the oxygen. Depending on the elemental composition of the compounds to be analyzed, other compounds, in addition to nitrogen and carbon monoxide, are found in the gaseous effluent from the reaction tube, among them acidic gaseous decomposition products. Since acid gases, for example hydrogen chloride or gaseous chlorine, can interfere with the determination of oxygen, it is necessary to remove them from the mixture of gases prior to oxidation of the CO to CO_2 in the oxidizer. Therefore, directly after the decomposition products, in admixture with nitrogen, leave the reaction tube, they pass through an alkaline absorbent where they are freed from acidic components.

Proceeding on the assumption that during the decomposition of halogen-containing compounds composed of C, H, O, and Hal in the presence of a sufficient amount of hydrogen the halogen must be liberated in the form of hydrogen halide, that is, a substance which has an acid character and is absorbed by alkali, we conducted experiments on the simultaneous determination of oxygen and halide. The determination was carried out in the following manner. A weighed sample was subjected to pyrolytic decomposition. The determination was carried out in a quartz tube, as in the determination of carbon and hydrogen by the rapid method [4], and the active decomposition products, which react more easily and rapidly with carbon than do the vapors of the original material, acted on the catalyst (platinized carbon, heated to 900°). This made it possible to decrease the carbon layer to 3 cm (Oita [5] used a contact layer 9 cm long) and to correspondingly decrease the length of the heating zone. The decomposition products were carried by the stream of nitrogen into the absorption apparatus, which was filled, as in the determination of C and H, with ascarite and anhydrone, where the hydrogen halide was absorbed. The carbon monoxide was then passed to a copper oxide tube heated to 100° and oxidized to CO_2, which was absorbed in the same absorption apparatus as was the halide previously. The oxygen was determined by the weight of the CO_2. The results, obtained in this manner, of the simultaneous determination of oxygen and halides are presented in Table 1.

Since the formation of hydrogen halide is due to the hydrogen formed in the reaction tube by the decomposition of the material being analyzed, as would be expected, in the analysis of material which does not contain hydrogen or which contains it in insufficient amount, difficulty was encountered. In these cases, the oxygen determination was good, but the results for halide were quite a bit too low. As we established later, a considerable portion of the halide was retained by the carbon, and was slowly and incompletely recovered even on lengthy passage of nitrogen through the reaction tube. This difficulty was overcome by the addition to the substance being analyzed of a material with a high content of hydrogen (for example, paraffin). This proved to be sufficient for quantitative liberation of halide in the form of hydrogen halide. It was also shown that, during the decomposition of the weighed portion of paraffin, the halide previously retained by the packing was quantitatively recovered from the reaction tube. Thus, for example, during an analysis of hexachloroethane conducted as usual, 57.06% chlorine was found instead of 89.89%. Subsequent passage of nitrogen through the

TABLE 1

Material	Weight, mg	Wt. Increase, mg		O, %		Cl, %	
		CO_2	HCl	found	difference	found	difference
Dimethyl ester of 4-chloro-5-hydroxy-1,2-decalindicarboxylic acid, $C_{14}H_{19}O_5Cl$ (11.89% Cl; 26.80% O)	10.120	7.368	1.217	26.58	−0.22	11.69	−0.20
	10.318	7.506	1.233	26.44	−0.36	11.62	−0.27
γ-Methyl-ω'-dichloroethylene-α-pyrone, $C_8H_6O_2Cl_2$ (34.64% Cl; 15.61% O)	13.582	6.082	4.818	15.96	+0.35	34.51	−0.13
Trichlorovaleric acid, $C_5H_7O_2Cl_3$ (51.96% Cl; 15.61% O)	12.883	5.654	6.837	15.88	+0.27	51.83	−0.13
	8.514	3.632	4.631	15.51	−0.10	51.70	−0.26
Chlorotridecanoic acid, $C_{13}H_{25}O_2Cl$ (14.29% Cl; 12.88% O)	17.916	6.231	2.718	12.65	−0.23	14.64	+0.35
	17.805	6.322	2.603	12.86	−0.02	14.19	−0.10

TABLE 2

Material	Weight mg	Weight of paraffin	Wt. Increase		O, %		Hal, %	
			CO_2	Hal	found	difference	found	difference
Hexachloroethane, C_2Cl_6 (89.89% Cl)	9.916	—	—	5.794	—	—	58.43	−31.46
	6.027	—	—	3.440	—	—	57.06	32.83
	5.839	6.737	—	5.346	—	—	89.03	−0.84
	5.276	6.272	—	4.802	—	—	89.20	−0.69
	6.735	8.330	—	6.254	—	—	89.09	−0.80
Tetrachloroethylene, C_2Cl_4 (85.53% Cl)	7.746	4.209	—	6.782	—	—	85.15	−0.38
Iodobenzoic acid, $C_7H_5O_2I$ (51.20% I; 12.90% O)	9.484	—	3.278	4.294	12.57	−0.33	44.92	−6.28
	10.270	—	3.719	4.601	13.17	+0.27	44.45	−6.75
	8.440	7.638	2.991	4.391	12.89	−0.01	51.62	+0.42
	9.081	4.289	3.182	4.701	12.74	−0.16	51.36	+0.16
Bromobenzoic acid, $C_7H_5O_2Br$ (39.77% Br; 15.93% O)	8.823	—	3.997	1.949	16.28	+0.35	28.82	−10.85
	8.734	4.366	3.800	3.493	15.82	−0.11	39.48	− 0.29
	8.420	4.209	3.626	3.462	15.66	−0.27	39.66	− 0.11

reaction tube four times for 30 minutes gave, respectively, 4.19, 4.65, 5.74, and 0.00% chlorine for a total of 71.58%, which is 18.31% less than the calculated value. Some paraffin was then decomposed in the reaction tube, and an amount of halide corresponding to 18.08% of the chlorine, based on the weight of the hexachloroethane previously decomposed, was recovered. Results which were too low by several percentage units were also obtained in the determination of iodine in iodobenzoic acid. In this case, liberation of elemental iodine was observed during decomposition of the sample, the iodine being easily detectable by the violet color of the vapors issuing from the reaction tube. Decomposition of iodobenzoic acid in the presence of paraffin gave correct results for both elements determined. The results of the determinations of halide and oxygen in the presence of paraffin are presented in Table 2.

The possibility of directly determining oxygen and halide simultaneously was first established by us. The halide can also be determined volumetrically. This extends considerably the application of the method. Moreover, in the presence of a sufficient amount of hydrogen and under the same conditions, it is apparently possible to determine simultaneously oxygen, sulfur, and halide.

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Institute of Elementoorganic Compounds
Academy of Sciences, USSR

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CONDENSATION OF ALDEHYDES WITH ACETIC ANHYDRIDE IN THE PRESENCE OF BORON ACETATE

V.K. Kuskov

(Presented by Academician S.I. Volfkovich, April 18, 1956)

The Perkins reaction (the synthesis of cinnamic acid and analogous syntheses) is interpreted by contemporary theory as a unique, individual case of crotonic condensation in the presence of a nucleophyllic reagent (usually a salt of the corresponding carboxylic acid [1]). It is still not clear why in the best variation of this reaction not less than a molecular amount, with respect to the aldehyde reactant, of the salt of the acid is required; i.e., it is not clear whether, in the classical synthesis, the sodium or potassium acetate is the catalyst and the acetic anhydride the reagent or the potassium acetate is the reagent and the acetic anhydride is required to tie up the water liberated by the reaction.

It has been established that the salt can enter into the Perkins reaction, for example, in the condensation of p-chlorobenzaldehyde with potassium acetate, and even acetic acid can enter directly into the reaction [2]. Recently, G.P. Miklukhin showed that the condensation of benzaldehyde with lead acetate is possible [3].

Universally accepted theory, based on numerous experimental investigations, proposes that acetic anhydride is the reagent in the classical variant of the Perkins reaction, although there is no direct proof of this up to the present. Attempts to carry out the synthesis of cinnamic acid in the presence of an acid are not described in the literature, although it is well known that crotonic condensation proceeds successfully in the presence of an acid in many cases.

In the present work, we carried out the condensation of benzaldehyde with acetic anhydride, as well as some analogous condensations, in the presence of "boron acetate", i.e., the tetraacetate of diboric acid [mesoboric acid] [4], $(CH_3COO)2BOB(OCOCH_3)_2$, which is prepared by the reaction of boric acid with acetic anhydride [5]. This compound is an aprotonic [Lewis] acid, stable in an acetic anhydride medium. The reaction proceeds homogeneously, and cinnamic acid is obtained in a yield of 75%. The amount of boron acetate is small, 0.1 of the weight of benzaldehyde; larger amounts decrease the yield of cinnamic acid and increase the yield of tarry products. Benzaldehyde does not condense directly with boron acetate. On heating a mixture of these reagents to 160-180°, a little cinnamic acid is obtained nevertheless; it is obvious, therefore, that above 121° boron acetate decomposes, and the decomposition products contain acetic anhydride which reacts with the benzaldehyde. Thus, boron acetate is a catalyst. Acetic anhydride is consumed in accordance with the reaction:

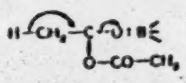
$$C_6H_5CHO + 2(CH_3CO)_2O \rightarrow C_6H_5CH = CHCOOCOCH_3 + 2CH_3COOH.$$

It is necessary to distill off the acetic acid formed during the course of the reaction; otherwise, it is necessary to increase by 1-2 times the amount of acetic anhydride, and the yield is decreased to 30-40%.

In contrast to the classical Perkins condensation, the reaction products do not contain unreacted benzaldehyde, but they do contain a light brown tar. The cinnamic acid was separated by extracting several times with 50% methanol, or aqueous methanol was added to hydrolyze the acetic anhydride, and the cinnamic acid was obtained by distilling the mixture under vacuum. At the conclusion of the reaction, the mixture can be treated with an alcohol to obtain the cinnamic acid ester. The tarry material obtained in the condensation is, at least partially, a product of the polymerization of cinnamic acid, as was shown by the following method. After exhaustive extraction of the cinnamic acid with 50% methanol, the tarry products were distilled under vac-

uum; the distillation products contained an appreciable amount of cinnamic acid which apparently was the result of depolymerization. Extraction of the tarry reaction products with hot 10% sodium hydroxide produced some benzoic acid.

By analogy with the catalytic action of other aprotonic [Lewis] acids, the following mechanism of the catalytic action of boron acetate can be proposed. The formation of the addition product



promotes the splitting of a proton from the methyl group and, thereby, an aldol condensation, i.e., the first stage of the reaction; the acetic anhydride promotes the elimination of water with the formation of cinnamic acid. m-Nitrocinnamic acid and the azolactone from benzaldehyde and hippuric acid were similarly prepared in the presence of boron acetate. Boric oxide can be used in place of boron acetate, the boric oxide, in conformity with literature data, being converted to boron acetate in the reaction mixture by reaction with the acetic anhydride.

Analogously to the Nef reaction [7], gradual heating of benzaldiacetate with boron acetate to 180° while distilling off the acetic acid also yields cinnamic acid; however, the yield does not exceed 35%.

$$C_6H_5CH(OCOCH_3)_2 \rightarrow C_6H_5CH = CH - COOH + CH_3COOH.$$

EXPERIMENTAL

Cinnamic Acid. 10.6 g (0.1 mole) of benzaldehyde, 20 g (0.2 mole) of acetic anhydride, and 1 g of boron acetate (or 0.45 g of boric oxide) were heated for 3 hours (4-5 hours with boric oxide) in a flask equipped with a herringbone dephlegmator (10 cm) on a sand bath until the distillation temperature was 120-122°. When the temperature in the flask reached 180°, the reaction was stopped; the residue in the flask was boiled several times with 20 ml of 50% methanol, filtered, and the cinnamic acid crystallized. 10.7 g was obtained; the yield was 72%. B.p. 132°. In another variation, after distilling off the acetic acid, the residue in the flask was mixed with 4 ml of methanol and 3 ml of water, heated 0.5 hour, and distilled under vacuum collecting the fraction at 170-200° at 25 mm Hg (partial decomposition occurred at the end). The cinnamic acid was washed with water and dried. 11.1 g was obtained; the yield was 75%.

Butyl cinnamate. The reaction was carried out as indicated above. After distilling off the acetic acid, the residue was heated (with a water trap added to the apparatus) while adding dropwise 25 ml of butyl alcohol over a period of 12-13 hours, the heating being conducted so that the temperature (180-200° interval) did not drop below 180° for 10 hours. About 1 ml of water was collected. The reaction mixture was diluted with benzene, washed with a 3% solution of soda, diluted with water, dried, and distilled under vacuum collecting the fraction boiling at 145-150 at 7 mm. 11 g (54%) of butyl cinnamate was obtained. Amyl cinnamate was prepared similarly.

m-Nitrocinnamic acid. 7.6 g (0.05 mole) of m-nitrobenzaldehyde, 15 g (0.15 mole) of acetic anhydride, and 2 g of boron acetate were heated on the bath for 13 hours to a temperature of 180°. The reaction mixture was cooled to 80° and decanted into 50 ml of water. The residue was dissolved in 100 ml of 3% ammonia, filtered, acidified with dilute sulfuric acid, filtered, washed with water, and crystallized from alcohol. 6.6 g (77%) of m-nitrocinnamic acid was obtained; m.p. 193-194°.

2-Phenyl-4-benzaloxazolone. 9 g (0.05 mole) of hippuric acid, 16 g (0.15 mole) of acetic anhydride, 5.3 g (0.05 mole) of benzaldehyde, and 1.9 g of boron acetate were heated 2 hours on a boiling water bath. Further treatment was carried out as usual [8]. The yield was 7.8 g (62%); m.p. 165-166° (from benzene).

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M.V. Lomonosov Moscow State University

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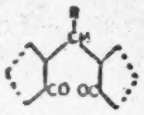
A SYNTHESIS OF ALICYCLIC 1,5-DIKETONES BASED ON MONO- AND DIARYLIDENECYCLANONES

M.N. Tilichenko and V.G. Kharchenko

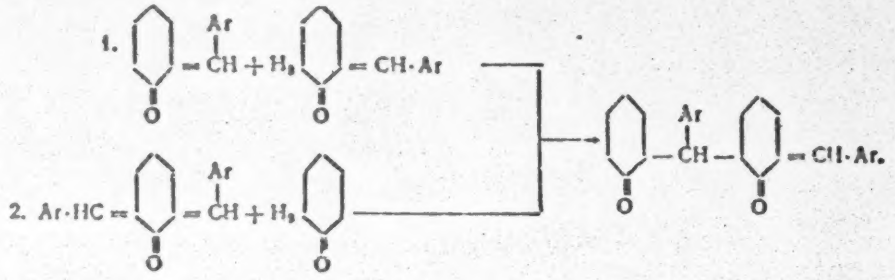
(Presented by Academician I.N. Nazarov, May 5, 1956)

Until recently, alicyclic 1,5-diketones of the form



were unknown. There have recently been described syntheses of several compounds of this type based on the condensation of cyclohexanone with formaldehyde [1], benzaldehyde and furaldehyde [2] and on the condensation of a series of cyclanones with trioxymethylene [3]. Further study of this group of interesting organic compounds requires, first of all, expansion of methods for their synthesis.

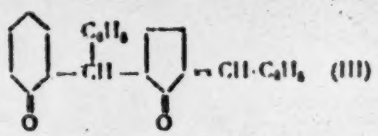
Below are described syntheses carried out by us according to Schemes (1) and (2):



$$\left(\text{Ar} = C_6H_5\ (\text{I}),\ \text{Ar} = \text{furyl}\ (\text{II})\right).$$

Both reactions proceed easily and quantitatively. The first of them can be considered as a dimerization of α-monoarylidenecyclanones. Such a conversion of these compounds is not described in the literature. The addition of cyclanones to diarylidenecyclanones also has not been studied by anyone. The type of reactions cited above is limited to the addition of only one molecule of cyclohexanone even when a large excess of the latter is introduced into the reaction mixture. A second molecule is added only under more severe conditions.

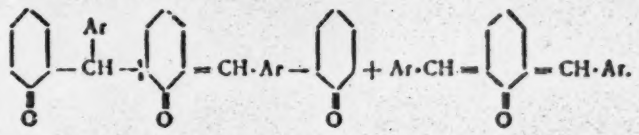
Cyclohexanone adds quite smoothly, molecule per molecule, to dibenzylidenecyclopentanone with the formation, obviously, of the diketone (III).



However, the addition of cyclopentanone proceeds less smoothly, and we have as yet been unable to obtain the corresponding diketone in a pure form.

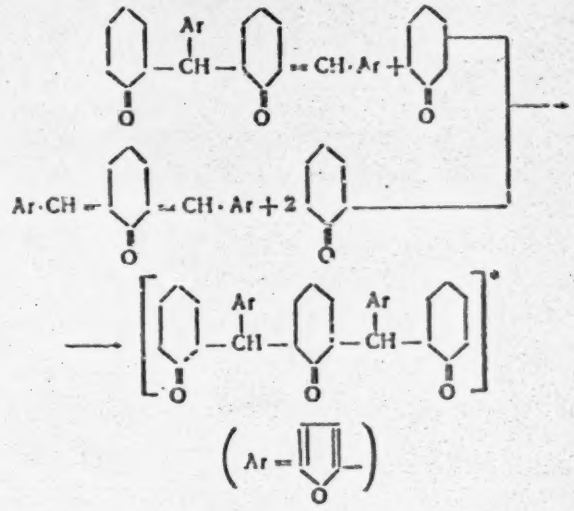
The structures of (I) and (II) were confirmed not only by the method of synthesis according to Scheme 2, but also by a series of transformations. Thus, both diketones easily form dioximes on reaction with hydroxylamine. On dry distillation at 245°, they split according to Scheme 3, which is the reverse of their synthesis according to Scheme 2. Such a type of thermal splitting is characteristic only of 1,5-diketones [4-8]. In the case of (II), the presence

3.



of a double bond in an α,β-position to the CO group was demonstrated by the addition of one molecule of cyclohexanone under conditions of the Michael reaction. The compound formed in this reaction was also obtained by the addition of two molecules of cyclohexanone to difurfurylidenecyclohexanone:

4.



The diketones (I), (II), and (III) are similar in physical characteristics: they separate from alcohol in the form of long prismatic rods which are readily soluble in benzene, difficultly soluble in alcohol, and very slightly soluble in petroleum ether.

Thus, the mono- and diarylidenecyclanones, which are widely available, can serve as the basis for the synthesis of a large group of polycyclic 1,5-diketones.

EXPERIMENTAL

Synthesis according to Scheme 1. The α-arylidenecyclohexanone was dissolved in the minimum volume of 1 N alcoholic NaOH. After several hours, the solution congealed into a crystallizing paste. The crystals were filtered and washed with alcohol and then with water. The yield of (I) and (II) was quantitative.

*The brackets indicate that the triketone is, possibly, only an intermediate compound, since, according to the rule of Rabe [9], it can isomerize into the corresponding ketol.

Synthesis according to Scheme 2. A mixture of the diarylidenecyclohexanone (1 mole), cyclohexanone (1 mole), and 1 N alcoholic NaOH, taken in the amount required for the solution of the diarylideneketone, was heated (5-6 minutes) until a homogeneous solution was obtained. The solution was then maintained for some time at 0°. In the experiments with dibenzylidenecyclohexanone, the solutions congealed after several hours into a crystalline paste. The crystals were separated as described above. The yield of (I) was quantitative. In the experiments with difurfurylidenecyclohexanone, the solutions did not crystallize on standing [(II) was more soluble than the difurfurylidenecyclohexanone], and the reaction product was separated by dilution with water.

The result was not changed by the introduction of 2-2.5 moles of cyclohexanone into the reaction mixture; (I) and (II) were obtained in the same yields.

Benzylidenebenzaldicyclohexanone (I). The long, white rods (from alcohol) melted with the liberation of alcohol of crystallization at 86-92°.

Found %: C 80.12; 80.06; H 7.74; 7.78. $C_{26}H_{28}O_2$ + 1 mole C_2H_5OH. Calculated %: C 80.38; H 8.13.

Recrystallization from a mixture of benzene and petroleum ether (1 : 2) gave rhombs with a constant melting point of 135-136° and which did not contain alcohol of crystallization.

Found %: C 83.56; 83.58; H 7.62; 7.54; M 364; 378. $C_{26}H_{28}O_2$. Calculated %: C 83.87; H 7.52; M 372.

By recrystallization from alcohol of the material melting at 135-136°, long rods melting at 86-92° were again obtained. The alcohol of crystallization was lost under vacuum only on heating (100°) for 28 hours.

Dioxime. The white crystalline powder melted at 194-195° (from a mixture of benzene and petroleum ether).

Found %: N 7.32; 7.07. $C_{26}H_{30}O_2N_2$. Calculated %: N 6.96.

Furfurylidenefuraldicyclohexanone (II). The long, white crystals, brought to constant weight under vacuum at 60-70°, melted at 128-130°; after recrystallization from a mixture of benzene and petroleum ether (1 : 2), the form of the crystals was unchanged, m.p. 130-131°.

Found %: C 75.32; 74.77; H 6.81; 6.77; M 344; 358. $C_{22}H_{24}O_4$. Calculated %: C 75.00; H 6.82; M 352.

Dioxime. Colorless rods with a constant m.p. of 158-159° (from benzene-gasoline mixture).

Found %: N 7.54; 7.19. $C_{22}H_{26}O_4N_2$. Calculated %: N 7.33.

3. Phenyl-α-cyclohexanonyl-α[α₁-benzylidenecyclopentanonyl]-methane (III)*. This compound was prepared from a mixture of 1 mole of dibenzylidenecyclopentanone and 2 or more moles of cyclohexanone under the conditions of synthesis 2. The long, white rods (from a 1 : 1 alcohol-benzene mixture) had constant melting points of 146-148° and 154-156°. The composition and molecular weights of both compounds were the same.

Found %: C 83.68; 83.50; H 7.41; 7.51; M 330; 344. $C_{25}H_{26}O_2$. Calculated %: C 83.80; H 7.26; M 358.

Thermal cleavage of (I) and (II). Upon distillation, both diketones cleaved according to Scheme 3 at 245°, cyclohexanone being distilled off slowly. The residue was a solid, black mass from which, only in the case of (II), was difurfurylidenecyclohexanone easily separated from a benzene solution (m.p. 143-145°; the m.p. of a mixture with known difurfurylidenecyclohexanone was not lowered). Upon distillation in an atmosphere of nitrogen and in the presence of ~0.1% hydroquinone, the depth of resinification was not decreased. The cyclohexanone obtained was identified by physical constants and by its semicarbazone (m.p. 164-165°, recrystallization from benzene; a sample of a mixture with known cyclohexanone semicarbazone melted at 164-165°). With a sufficiently long distillation, the yield of cyclohexanone approached quantitative in both cases.

*With the participation of E.V. Leiman.

Addition of cyclohexanone to (II). The addition was accomplished by heating a solution of (II) and cyclohexanone in 1 N alcoholic NaOH at 78-80°. White, hexagonal crystals were precipitated during heating of the solution. The crystals, filtered and washed with alcohol, melted with decomposition at 236-237°. The material was insoluble in alcohol, ether, and acetone, difficultly soluble in benzene and nitrobenzene, and soluble in pyridine and dioxane.

Found %: C 74.50; 77.77; H 7.52; 7.72; M (from dioxane) 461; 455. $C_{28}H_{34}O_8$. Calculated %: C 74.66; H 7.55; M 450.

This same product was obtained by the addition of 2 moles of cyclohexanone to 1 mole of difurfurylidenecyclohexanone under similar conditions (the identity of the two substances was confirmed by mixed melting point).

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TRANSFORMATIONS OF ORTHO- AND PARA-NITROTOLUENES IN ALKALINE MEDIUM

M.N. Shchukina and G.S. Predvoditeleva

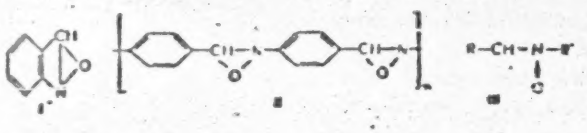
(Presented by Academician P.L. Knunyants, April 11, 1956)

One of the most satisfactory reactions for the preparation of p-aminobenzaldehyde is its formation from p-nitrotoluene by the action of sulfur in an aqueous alcoholic solution of sodium hydroxide [1]. The p-aminobenzaldehyde is separated in the form of a polymer with azomethine bonds in 80% yield. p-Toluidine (about 10%) is also formed. However, in spite of the practical value of this reaction and the accessibility of the starting materials, the mechanism is still not clear.

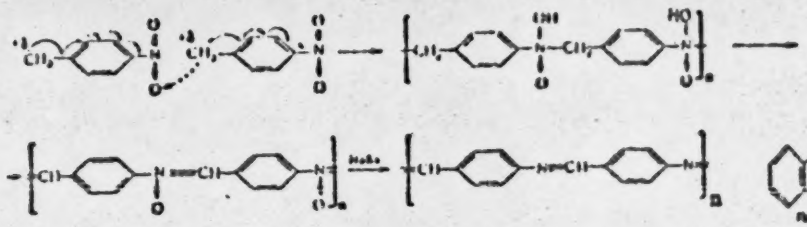
Since p-nitrotoluene undergoes a series of different reactions under the action of alkali, it was expedient to study these processes and to compare them with the reactions of o-nitrotoluene under similar conditions. It is known that the composition and relative amount of products of the reaction of p-nitrotoluene with alkali depends, to a great extent, on temperature, heating time, and alkali concentration [2]. By changing the reaction conditions, azo- and azoxy-toluene, dinitrostilbene, or dinitrodibenzyl can be obtained [3]. However, in all cases of continued heating of p-nitrotoluene with alcoholic or aqueous alcoholic alkali the basic reaction product is a brownish red, amorphous substance, the structure of which has not been established. Also depending on the reaction conditions, different substances are obtained by the action of an alkaline solution on o-nitrotoluene: o,o'-dinitrodibenzyl, o-azotoluene, and, by continued action of aqueous alcoholic alkali, anthranilic acid, together with o-azo- and o-azoxybenzenecarboxylic acids [4]. Scholl [5] proposed a mechanism for the formation of anthranilic acid from o-nitrotoluene through an intermediate product – anthranil – which was formed by this reaction (I).

It can be assumed that the transformations of p-nitrotoluene under the influence of alkali proceed similarly to the transformations of o-nitrotoluene, i.e., through the formation of an intermediate compound of the type of anthranil. In the case of p-nitrotoluene, the formation of such a compound in one molecule is impossible, but a similar interaction is permissible among molecules with the formation of the polymer (II).

At present, the nitrone formula (III) is universally accepted for compounds containing a similar grouping (N-ethers of benzaldoximes).



If a reducing agent (sodium polysulfide, obtained by the solution of sulfur in alkali) is present in the reaction mixture, the nitrone polymer formed is reduced to a compound with azomethine bonds, which is later hydrolyzed to p-aminobenzaldehyde. Thus, the mechanism of the formation of p-aminobenzaldehyde from p-nitrotoluene can be represented as follows:



Comparing the chemical properties of the nitrones and anthranil [6], it can be concluded that they correspond almost completely and that the most probable of all the proposed formulas of anthranil is the nitrone formula (IV). Accordingly, on the basis of our proposed reaction mechanism, the reaction of o-nitrotoluene with sulfur and alkali would be expected to yield o-aminobenzaldehyde. The reaction of o-nitrotoluene in alkaline solution in the presence of sulfur was studied, and it was found that, under conditions leading to the formation of p-aminobenzaldehyde from p-nitrotoluene, o-aminobenzaldehyde (14%) and o-toluidine were formed from o-nitrotoluene. When the solution of sulfur in alkali was added only after boiling the o-nitrotoluene with 20% aqueous alcoholic alkali for several hours, 2-indazylbenzyl alcohol was formed (15%).

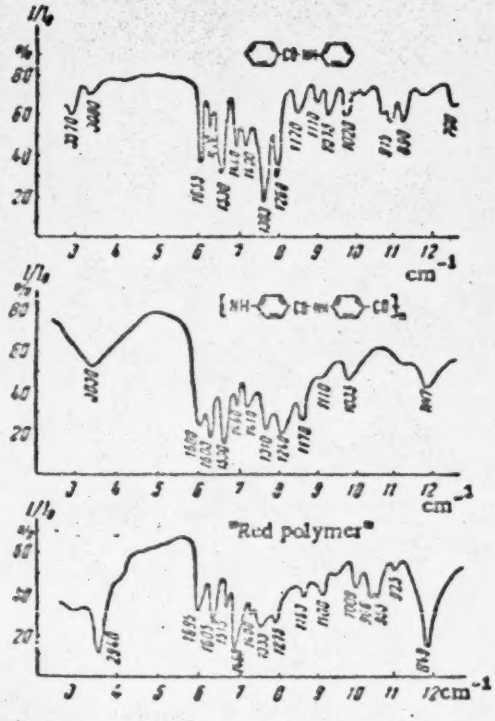


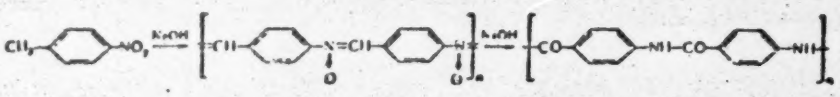
Fig. 1.

In order to confirm the possible existence of intermediate compounds of the nitrone type during the preparation of o- and p-aminobenzaldehydes from o- and p-nitrotoluenes, the action of a solution of sulfur in alkali on anthranil and on certain nitrones was investigated. And, indeed, o-aminobenzaldehyde, along with anthranilic acid, was obtained from anthranil, benzalaniline was obtained from phenyl-N-phenylnitrone, and an anhydropolymer of p-aminobenzaldehyde, along with p-toluidine, was obtained from p-nitrophenyl-N-p-tolylnitrone.

Since it could be assumed that the first stage in the preparation of p-aminobenzaldehyde is the formation of polymer with nitrone groups, the brownish red amorphous substance formed by the action of alkali on p-nitrotoluene ("red polymer") was investigated. This substance is extremely inert chemically. It is not hydrolyzed by acids or alkalies of various concentrations, and it is neither oxidized nor reduced. In order to clarify the structure, it was investigated spectroscopically in the infrared region. In view of the absence from the literature of data on the infrared spectra of nitrones and on the absorption band of the N → O bond, we investigated the spectra of a series of nitrones. For this purpose, butyl-N-methylnitrone (the first member of the aliphatic nitrones, which are not described in the literature) was synthesized and its infrared spectrum studied, as were the N-oxides of pyridine and trimethylamine. Thus, it was shown that these three compounds are characterized by two intense bands which occur in the spectra of the aromatic nitrones in the regions 1185-1250 and 920-950 cm^{-1}. It may be assumed that these intense bands are connected with vibrations in which the N → O group takes part. This conclusion is confirmed by Raman data on trimethylamine N-oxide [7], the authors noting a line at 947 cm^{-1} which they ascribed to vibrations of the N → O bond. The absorption band lying in the 920-950 cm^{-1} region of the spectra of the nitrones and N-oxides can be related to the symmetrical vibration of the $-C=N-$ group; the band in the 1250-1185 cm^{-1} region is apparently connected with the asymmetrical vibration of this same group. The indicated bands lie in the region of single bonds, which can be considered as physical confirmation of the semipolar character of the N → O bond in nitrones.

An examination of the spectra of "red polymer" showed that the absorption band characteristic of N → O bonds in nitrones is absent. This circumstance as well as the fact that this polymer, in contrast to nitrones, is neither hydrolyzed nor oxidized leads to the conclusion that the groups connecting the aromatic groups are not nitronic and that under the influence of alkali deeper changes take place.

It is well known [8] that certain nitrones undergo a Beckmann rearrangement into acid amides under the influence of alkaline agents. We found that by the action of aqueous alcoholic alkali on p-nitrophenyl-N-p-tolylnitrone an infusible polymer is formed which, in contrast to the original nitrone, is not hydrolyzed and is not changed by the action of an oxidizing agent. By the action of piperidine on this same nitrone, p-nitrobenzotoluide was obtained. This permits the assumption that the first product of the action of alkali on p-nitro-toluene is a nitrone which then undergoes a Beckmann rearrangement. The nitrone group is thereby converted to an amide, and the "red polymer" formed is a polyamide:



The red polymer is extremely inert, and we were unable to hydrolyze it by various methods for amide cleavage. Therefore, in order to detect the amide groups, it was investigated spectroscopically (Figure 1). For comparison, a similar polyamide was synthesized by a method leaving no doubt as to the structure of the substance obtained. For this purpose, p-aminobenzoic acid was subjected to protracted treatment with thionyl chloride with heating. The polyamide formed, the composition of which was confirmed by elemental analysis, had properties similar to those of "red polymer". A comparative study of the infrared spectra of this polyamide, "red polymer", and benzanilide showed them to be in close agreement.

It is well known that the absorption band of the carbonyl group in amides lies in the 1660-1680 cm^{-1} region. It can be considered that this group in benzanilide corresponds to the absorption band at 1655 cm^{-1}; in the polyamide obtained from p-aminobenzoic acid the band is 1680 cm^{-1}; in "red polymer" the band is at 1695 cm^{-1}.

Thus, the spectral data confirm the polyamide structure of "red polymer" and also the scheme proposed by us for the transformation of p-nitrotoluene under the action of sulfur and alkali.

As has already been noted, the intermediate product in the transformation of o-nitrotoluene under the influence of alkali is anthranil. Under the influence of alkali it is converted into anthranilic acid. It can be assumed that this conversion proceeds similarly to the conversion of nitrones through the formation of an inner amide of anthranilic acid – an unstable β-lactam – which immediately hydrolyzes to the acid. The conversion of o-nitrotoluene under the influence of alkalies of various concentrations and of an alkaline solution of polysulfides and the preparation thereby of different substances can be represented as follows. Anthranil is formed from o-nitrotoluene under the influence of alkali; the former then undergoes various reactions depending on conditions. Under the influence of 40-50% aqueous alcoholic alkali it is converted into anthranilic acid. If it is treated with a dilute (8%) aqueous alcoholic solution of polysulfides, some part of the anthranil is reduced to p-aminobenzaldehyde. The formation of o,o'-azoxy- and o,o'-azobenzenecarboxylic acid and also of 2-indazylbenzyl alcohol can be explained by the following course of reaction: the anthranil formed is hydrolyzed by the action of 20% aqueous alcoholic alkali similarly to certain nitrones, which are converted into o,o-azoxybenzaldehyde in an alkaline medium. In the alkaline medium, the latter can undergo disproportionation into o,o'-benzylcarboxylic acid and o,o'-azoxybenzyl alcohol. When a reducing agent is present in the reaction mixture (sodium polysulfide), the azoxy compound can be converted into an azo compound, and, as is well known [9], o,o-azobenzyl alcohol is easily converted into 2-indazylbenzyl alcohol, which was also isolated.

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S. Ordzhonikidze All-Union Chemical-Pharmaceutical Research Institute

INVESTIGATION OF THE n-PARAFFINIC HYDROCARBONS IN THE 200-250° FRACTION OF NORII PETROLEUM BY MEANS OF UREA

Kh. I. Areshidze and E. M. Benashvili

(Presented by Academician A. V. Topchiev, April 18, 1956)

A number of papers ([1-12] and others) have been devoted to establishing the individual hydrocarbons occurring in different petroleums.

Georgian petroleum has been little studied in this regard. Only in a paper by F. Beilshtein and A. Kurbatov [4] is there an indication that petroleum from the Krasny wells (Tsarsky wells) contains n-pentane and isopentane with a b.p. of 30°. It must be assumed that this investigation [4] dealt with Mirzaani petroleum.

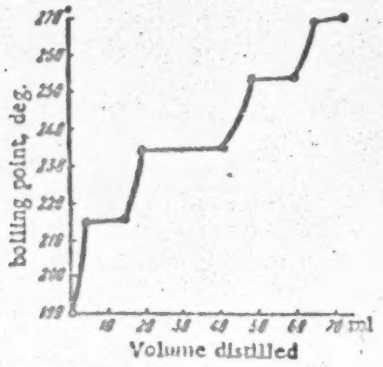

Fig. 1

TABLE 1

Temp., °C	Quantity, ml	Yield, % vol. of charge	n_D^{20}
194—215	4.3	4.6	1.4225
215—216	10.0	10.6	1.4219
216—234	5.3	5.6	1.4292
234—235	20.9	22.2	1.4250
235—253	8.0	8.5	1.4350
253—254	11.2	11.9	1.4295
254—269	5.4	5.7	1.4395
269—270	7.1	7.5	1.4310
Residue and loss	21.8	23.2	
Total	94.0		

In the present work, urea was used for the separation of normal paraffinic hydrocarbons. The ability of urea to form crystalline products by interaction with normal paraffinic hydrocarbons and other organic compounds having a normal hydrocarbon chain was discovered by Bengen [13] and has since been the subject of investigation by a number of authors [14, 15]. The paraffinic hydrocarbons in the kerosene fraction of certain Soviet petroleums were first investigated by this method by L. M. Rosenberg [16]. V. A. Nekrasova and N. I. Shulkin [17] isolated n-undecane from the 190-200° fraction of a Crimean petroleum by means of urea.

By means of urea, we isolated and identified low-boiling n-paraffins, such as nonane and n-decane, from the 150-200° fraction of Mirzaani petroleum; n-undecane was shown to be present in the same fraction [18].

A. V. Topchiev, L. M. Rosenberg et al, carried out a differential thermal investigation of adduct formation of urea with n-paraffins.

We established that the 200-250° fraction of Norii petroleum contains 29.3% paraffinic hydrocarbons, of which 2.5% are compounds of normal structure. It was of interest to determine the possibility of a quantitative

TABLE 2

Hydrocarbons	Literature data						Our data							
	B.p., °C	F.p., °C	n_D^{20}	d_4^{20}	Max. aniline point, °C	Mol. wt.	MR_D	B.p., °C	F.p., °C	n_D^{20}	d_4^{20}	Max. aniline point, °C	Mol. wt.	MR_D
Dodecane	216.2	−9.6	1.4216	0.7487	83.7	170.33	57.76	215—216	−10.0	1.4219	0.7492	82.9	168.56	57.16
Tridecane	235.5	−6.0	1.4255	0.7562	87.0	184.35	62.39	234—235	−6.5	1.4250	0.7569	85.9	183.77	62.73
Tetradecane	253.8	+5.5	1.4291	0.7620	89.5	198.38	67.07	253—254	+4.9	1.4295	0.7631	88.1	197.90	66.92
Pentadecane	270.0	+9.8	1.4319	0.7683	92.0	212.41	71.69	269—270	+9.5	1.4310	0.7685	90.7	210.51	70.86

Isolation of the n-paraffins from a complex mixture of hydrocarbons in which their content totaled 2.5% or 3.8% of the dearomatized fraction.

EXPERIMENTAL

Norii petroleum was used for the investigation; after topping to 200°, the 200-250° fraction was isolated (by fractionation of the residue boiling above 200°) under vacuum at a pressure of 20 mm Hg.

The fraction investigated was washed with 70% sulfuric acid, 10% soda, and distilled water to remove the nonhydrocarbon components which are encountered as traces in petroleum fractions and which are inhibitors for adduct formation with urea [15]. The presence of these nonhydrocarbon components also affects the accuracy of the group composition determination, since the coefficients used for this purpose have been established for hydrocarbon mixtures.

Dearomatization of the 200-250° fraction was carried out by means of sulfuric acid having a specific gravity of 1.84. The complete removal of aromatic hydrocarbons was checked by the formalin reaction of A. M. Nastyukov [20].

The next step was the isolation of the normal paraffinic hydrocarbons with urea, the process being carried out as supplemented and refined by L. M. Rosenberg [16].

According to the group composition, the dearomatized 200-250° fraction contained 38.5% paraffinic hydrocarbons.

The amount of urea used was determined on the basis of the average molecular weight of the fraction, which was equivalent to tridecane, 10.5 moles of urea being used for each mole of hydrocarbon.

The n-paraffinic hydrocarbons isolated were extracted with ethyl ether. After elimination of the ether, the mixture of n-paraffins, in the amount of 94 ml, was fractionated on a column of 45 theoretical plates at a pressure of 10 mm Hg. The distillation curve is presented in Figure 1. In Table 1 are presented certain properties of these fractions.

From the data presented, it can be seen that the individual n-paraffinic hydrocarbons were concentrated in fractions boiling at 215-216°, 234-235°, 253-254°, and 269-270°.

In Table 2 are presented the physicochemical properties of the hydrocarbons isolated by us along with the literature data [21].

Spectroscopic investigation of the fractions indicated above was also carried out.* Hydrocarbons of normal structure having the composition C_{12}, C_{13}, C_{14} and C_{15}, with a purity of 95%, were detected by means of the infrared spectra (in the region corresponding to CH_2 and CH_3, 3.3-3.6).

As a result of this investigation, the following n-paraffinic hydrocarbons were isolated from the 200-250° fraction of Norii petroleum:

* This part of the work was carried out by Yu. P. Egorov, for which our appreciation is expressed.

dodecane, tridecane, tetradecane, and pentadecane, these being identified by physical properties and also by infrared analysis; the presence of n-decane and n-undecane in the 194-215° fraction was established by this same method.

P. G. Melikishvili Institute of Chemistry
Academy of Sciences Georgian SSR

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CONTRIBUTION TO THE PROBLEM OF THE MECHANISM OF THE TRANS-EFFECT

S. S. Batsanov

(Presented by Academician I. I. Chernyaev, March 22, 1956)

From the time of the discovery by I. I. Chernyaev [1] of the trans-effect rule, the problem of the mechanism of this phenomenon has remained in the purview of theoretical chemists. Up to the present, many attempts at a theoretical explanation of the nature of the reciprocal effect of atoms of the inner sphere of complex compounds have been made; we will dwell here only on the basic ideas.

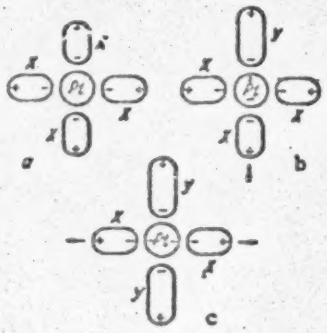

Fig. 1

In 1935, B. V. Nekrasov attempted an explanation of the trans-effect by means of a polarization concept. The course of his reasoning was thus. During the course of the formation of a complex, for example, of divalent platinum, the addend X will be polarized. Since the substituents are alike, the effect of the dipoles on the central atom (c. a.) of the complex will be symmetrical (Figure 1,a). In the case of addends of different types, for example, 3X and Y, the effect of the dipoles becomes asymmetrical . If the dipole Y is greater than X, the platinum becomes an induced dipole under its effect, and the greater the difference between dipoles X and Y, the greater the Pt dipole. Interaction of the charges on the central atom and the ligand in the trans-position to Y leads to a weakening of the Pt-X bond as a consequence of the expulsion of X from the inner sphere of the complex compound (Figure 1,b).

It can be shown that such an approach leads to contradiction with experiment upon its further development. If in the trans-position to Y is another such addend, Y, it is easily seen that under the influence of the dipoles (Y> X) the charges in the central atom will be distributed as shown in Figure 1,c. This should lead to the expulsion of X, while actually the trans-bond Pt–Y is weakened as before.

In the course of an experimental study of reactions in the inner sphere of complex compounds from the point of view of the trans-effect [3], it was found that the trans-effect of atoms is closely connected with the nature of the chemical bond c. a. – addend. Precisely, the trans-effect of the addend is greater the more covalent is its bond with the central atom. Thus, there is a distinct parallelism between the accumulation of electrons in the interatomic space and the trans-effect.

We should note here particularly the work of A. D. Gelman [4], who experimentally observed the great trans-effect of ethylene. Gelman connected this property with a special form of "oxidation" of the inner complex, because of which a part of the electron cloud of the platinum is drawn to the ethylene. It is as though such a process converts the divalent platinum to tetravalent. In support of this position can be cited the apparent increase in coordination number of ethylenic compounds of divalent platinum [5].

I. I. Chernyaev and A. D. Gelman [6] were inclined to account for the trans-effect of the addend by the degree of its covalency with the central atom. Considering the unsaturated molecule as simultaneously a donor and an acceptor of electrons, these authors considered possible the formation of covalent double bonds with the central atom. The high electron density in the locale of the double bond is the cause of the increased trans-effect.

Chatt [7] extended this idea to the trans-effect of addends in general. According to Chatt, in the case of an addend with a strong trans-effect, not only the electrons donated by the addend, but also the electrons supplied by the platinum participate in the chemical bond. This results in the formation of the double bond Pt=B (Figure 2,a). Simultaneously with the strengthening of the bond (and precisely because of it) the bond of the Pt with the addend (A) in the trans-position to B is weakened. Thus, according to Chatt, the process of the trans-effect is in contradiction to that which was proposed by B. V. Nekrasov; in the case of a addend with a strong trans-effect, the electrons are drawn to it and there is a decrease in the electron density on the other side of the central atom.

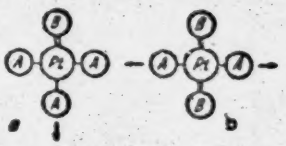

Fig. 2

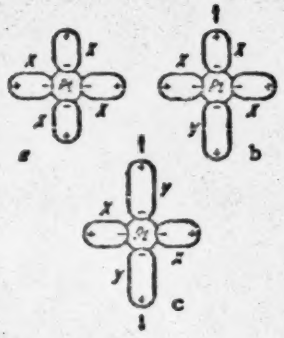

Fig. 3

It is not difficult to show that this purely "covalent" approach does not stand up under further development. If the same experiment is carried out with the Chatt model as with the Nekrasov model, we immediately arrive at a contradiction with experiment. According to Chatt, placing in the trans-position to A another such addend we should have an equal strengthening of the Pt–B bonds from both opposite sides (these, of course, will be one-and-a-half, not double, bonds), while the energy of the Pt–A bonds remains as before (Figure 2,t). In other words, in such a distribution the Pt–A bonds will be weaker than the Pt–B bonds; i.e., again the atoms in the cis-position to the more active addends will be expelled. It should be noted that, according to structural analysis data [8], the Pt–Cl bond distance in complex compounds is close to the sum of the covalent radii (usually barely larger), while for the double bonds, which the theory of Chatt requires, the distance should be appreciably less than the ordinary covalent single bond length.

TABLE 1

	R_D		
	R_{at}	R_{ion}	ΔR_s
F	0.81	2.44	1.63
Cl	5.84	9.06	3.22
Br	8.74	12.66	3.92
I	13.95	19.21	5.26
O	2.01	6.95	2.47
OH	2.55	4.76	2.21
NO_2	6.71	8.95*	2.24
NO_3	9.03	11.01	1.98
CO_3	7.70	12.14	2.22
SO_4	11.09	14.72	1.81
S	7.92	22.70	7.49

* For the crystalline state.

Thus, two opposite approaches, the electrostatic and the covalent, yield the same result which is contrary to experiment. The reason is that the bases of both of these models lie in the same false concept: the c. a. – addend bond is stronger the greater the trans-effect possessed by the given addend irrespective of the opposing substituent.

Let us return to the Nekrasov model. During the approach of the X ions to the Pt^{+2} ion, a dipole arises at first. But the further approach of this dipole toward the platinum will be accompanied, not by a weakening of the electron density on this side of the platinum (as assumed by B. V. Nekrasov), but, on the contrary, by an increase, since a chemical bond is formed. For this reason, at the site of the Pt–X bond we obtain a negative charge which will interact with a charge of the same sign and value on the opposite side, in the case of a homogeneous complex (Figure 3,a), or with a greater or

lesser charge, in the case of a heterogeneous complex (Figure 3,b). The occurrence in trans-positions of two of the same atoms opposing each other does not lead to contradiction with experiment in this model, since in accord with the strengthening or weakening of the charge of these two atoms, they (and not the cis-neighbors) will experience the greater mutual repulsion (Figure 3,c). This latter, obviously, will be more marked the more covalent the c.a. – addend bond. Finally, in the case of ethylene or any other unsaturated molecule, electrons will accumulate in the interatomic space owing to inner sphere oxidation, and we obtain an unusual dipole (a quadrupole) which will expel its trans-partner with the same success as a "real" dipole.

A quantitative nature can be given to the approach developed in the present article. For this purpose, it is expedient to use the refraction of the valence electrons of the addends. It is a fact that the higher the polarizability of the electrons, the greater will be their effective negative charge. For this reason, the refraction of an ion or atom increases in accordance with the increase in ionic or atomic radius [9]. The refraction of a free electron is obviously equal to infinity, and according to Chernyaev [1], a free electron possesses the greatest trans-effect.

In the case of a pure covalent bond (compounds of tetravalent platinum, according to x-ray structural data [8], approach this sufficiently closely), the refraction of the bonding electrons will be proportional to the difference in the refractions of the ions and the corresponding atoms. In Table 1 are compared the atomic [10] and ionic [11] refractions of typical addends, the difference in refractions being calculated on the basis of one electron.

It is seen from the table that the refraction of the bonding electrons increases in the series F^-, SO_4^{--}, NO_3^-, OH^-, CO_3^{--}, NO_2^-, O^{--}, Cl^-, Br^-, I^-, S^{--}. It is obvious that for such molecules as H_2O and NH_3 $\Delta R = 0$; i.e., they fall at the first of the series. This series is in agreement with the well-known trans-effect series [1]. The NO_2 group is an exception to the series of Chernyaev. However, both chemical and physical data indicate that the nitro group has less effect than chlorine in tetravalent platinum compounds.

Thus, the series of bonding electron refractions, which parallels the effective negative charges of the groups, adequately reflects the capacity of the atoms toward the trans-effect. In this light, it would be of interest to determine the molecular refraction of ethylene-containing complexes, to calculate from them the refractivity ethylene, and to compare this value with the refractivity of free ethylene.

The data cited in the present paper show that the correct explanation of the trans-effect is possible only by simultaneous consideration of electrostatic and "covalent" effects, while attempts to explain the trans-effect from either of these extreme positions leads to results which are in contradiction with experiment.

M. V. Lomonosov Moscow State University

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APPLICATION OF THE HAMMETT FORMULA TO ELEMENTOORGANIC COMPOUNDS. IONIZATION CONSTANTS OF PHOSPHORUS ACIDS

Associate Member of the Academy of Sciences M. I. Kabachnik

The Hammett formula, which defines the rate constant of chemical reactions (or the equilibrium constant) of benzene derivatives with substituents in the para- or meta-position to the reacting group as a function of the rate constant (or equilibrium constant) of the unsubstituted substance [1], has been verified experimentally for

$$\log \frac{K}{K_0} = \rho\sigma, \qquad (1)$$

a large number of cases [2]. The application of the Hammett formula to reactions of aliphatic compounds has met with difficulty: the effect of substituents located far from the reacting center is poorly transferred along the saturated chain, and the effect of those located close is complicated by steric factors [3]. Elementoorganic compounds of elements of the second and succeeding periods of the periodic system appear to constitute a field of new

TABLE 1

Ionization Constants of Aliphatic Acids, R'R"POOH, in Water

No.	R'	R"	pK_1	pK_2	Lit.	No.	R'	R"	pK_1	pK_2	Lit.
1	H	H	1.00	...	[4]	15	C_2H_5	HO	2.59	8.19	[8]
2	H	HO	1.41	6.70	[5]	16	i-C_3H_7	HO	2.70	8.43	[8]
3	HO	HO	1.97	6.82	[6]	17	i-C_3H_7	HO	2.66	8.44	[8]
4	CH_3O	HO	1.54	6.31	[6]	18	sec-C_4H_9	HO	2.74	8.48	[8]
5	C_2H_5O	HO	1.60	6.62	[6]	19	tert-C_4H_9	HO	2.79	8.88	[8]
6	C_3H_7O	HO	1.88	6.67	[6]	20	$C_{12}H_{25}$	HO	2.80	8.40	
7	C_4H_9O	HO	1.89	6.84	[6]	21	$ClCH_2$	HO	1.40	6.30	[10]
8	CH_3O	CH_3O	1.25	...	[7]	22	Cl_2CH	HO	1.14	5.61	[10]
			1.29		[6]	23	Cl_3C	HO	1.63	4.81	[10]
9	C_2H_5O	C_2H_5O	1.37	...	[7]	24	$BrCH_2$	HO	1.14	6.52	[10]
			1.39		[6]	25	ICH_2	HO	1.30	6.72	[10]
10	C_3H_7O	C_3H_7O	1.52	...	[7]	26	$HOCH_2$	HO	1.91	7.15	[10]
			1.59		[6]	27	F_3C	HO	1.18	3.03	[5]
11	C_4H_9O	C_4H_9O	1.72	...	[6]				1.17	3.92	[11]
12	CH_3	HO	2.38	7.74	[8]	28	CH_3	CH_3	3.08	...	[8]
			2.35	7.10	[9]	29	C_2H_5	C_2H_5	3.29	...	[8]
			2.48	7.34	[5]	30	C_3H_7	C_3H_7	3.48	....	[8]
13	C_2H_5	HO	2.43	8.05	[8]	31	i-C_3H_7	i-C_3H_7	3.56	...	[8]
			2.45	7.85	[9]	32	C_4H_9	C_4H_9	3.41	...	[8]
14	C_3H_7	HO	2.49	8.18	[8]	33	tert-C_4H_9	tert-C_4H_9	4.24	...	[8]

and possibly, broad application of the Hammett formula; the large, easily polarized electron sphere of the atoms of these elements should transfer well the mutual effects of the groups bonded to the central atom; on the other hand, the large radii of these atoms should promote a decrease in the steric effect.

TABLE 2

Ionization Constants of the Aromatic Acids $RPO(OH)_2$ in Water and in 50% Alcohol

No.	R	In water		In 50% alcohol		Lit.
		pK_1	pK_2	pK_1	pK_2	
34	C_6H_5	1.83	7.07	3.15	8.28	[12]
35	m-$CH_3N^+H_2C_6H_4$	1.10	6.60	—	—	[13]
36	p-$(CH_3)_3N^+HC_6H_4$	1.10	—	—	—	[13]
37	m-$C_6H_5N^+H_2C_6H_4$	1.10	—	—	—	[13]
38	p-$NO_2C_6H_4$	1.24	6.23	2.50	7.42	[12]
39	m-$NO_2C_6H_4$	1.30	6.27	2.57	7.43	[12]
40	p-$NH_2SO_2C_6H_4$	1.42	6.34	2.52	7.52	[12]
41	β-HOOCC$_6H_4$	1.50	—	2.80	—	[12]
42	m-FC_6H_4	1.54	6.69	2.85	7.96	[12]
43	m-ClC_6H_4	1.55	6.65	2.83	7.94	[12]
44	m-HOOCC$_6H_4$	1.55	—	2.83	—	[12]
45	p-BrC_6H_4	—	6.83	2.88	8.01	[12]
		1.60	6.60	—	—	[13]
46	p-ClC_6H_4	1.66	6.75	2.93	7.99	[12]
47	m-HOC_6H_4	1.74	6.75	2.93	7.99	[12]
48	p-$CH_3C_6H_4$	1.98	7.24	3.32	8.38	[12]

No.	R	In water		In 50% alcohol		Lit.
		pK_1	pK_2	pK_1	pK_2	
49	p-HOC_6H_4	1.99	7.25	3.14	8.49	[12]
50	p-$C_2H_5OC_6H_4$	2.08	7.28	3.37	8.49	[12]
51	p-$CH_3OC_6H_4$	2.09	7.19	—	—	[12]
52	p-$C_2H_5SC_6H_4$	—	—	3.14	8.22	[12]
53	p-$CH_3CONHC_6H_4$	—	7.10	3.15	8.24	[12]
54	3,4-$CH_2O_2C_6H_3$	—	7.15	3.21	8.33	[12]
55	p-^-OOC-C_6H_4	—	6.89	—	8.15	[12]
56	m-$^-OOCC_6H_4$	—	6.89	—	8.15	[12]
57	m-$NH_2C_6H_4$	—	7.16	—	8.31	[12]
58	m-$C_6H_5NHC_6H_4$	—	7.24	—	—	[12]
59	m-$CH_3NHC_6H_4$	—	7.30	—	—	[12]
60	m-$C_6H_5NH_2^+C_6H_4$	—	7.22	—	—	[12]
61	m-$NH_3NHC_6H_4$	—	—	—	8.22	[12]
62	p-$NH_2C_6H_4$	—	7.53	—	—	[12]
63	p-$NH_3NHC_6H_4$	—	7.54	—	—	[12]
64	p-$CH_3NHC_6H_4$	—	7.58	—	—	[12]
65	p-$(CH_3)_2NC_6H_4$	—	7.35	—	—	[12]

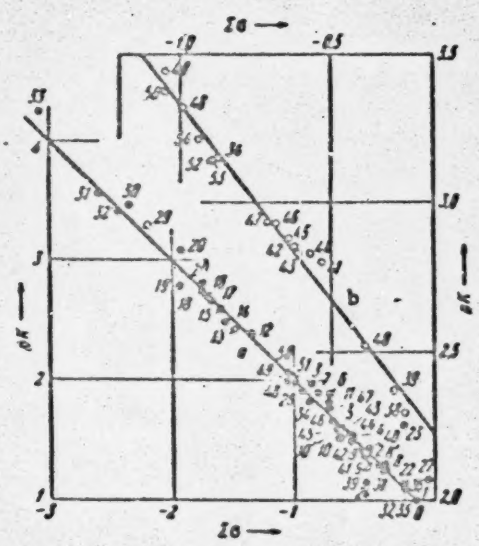


Fig. 1. Variation in pK with $\Sigma\sigma$. a) for acids of the type R'R"POOH in water; b) for acids of the type $RPO(OH)_2$ in alcohol (first stage of ionization).

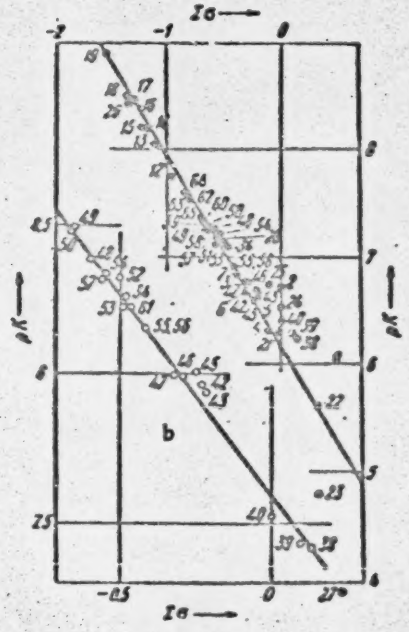


Fig. 2. Variation in pK with $\Sigma\sigma$ for the second stage of ionization of acids of the type $RP(O)(OH)_2$. a) in water; b) in alcohol.

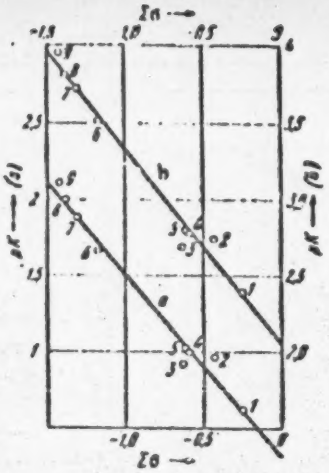


Fig. 3. Variation in pK with $\Sigma\sigma$ for acids of the type R'R"PS(OH): a) in water; b) in alcohol.

TABLE 3

Ionization Constants of the Acids R'R"PS(OH) in Water and in 80% Alcohol

No.	R'	R"	pK in water	pK in 80% alcohol	Lit.
1	CH_3O	CH_3O	0.62	2.30	
2	C_2H_5O	C_2H_5O	0.57	2.74	
3	C_3H_7O	C_3H_7O	0.92	2.69	
4	[illegible]	[illegible]	1.06	2.77	
5	$i\text{-}C_3H_7O$	$i\text{-}C_3H_7O$	1.03	2.98	
6	CH_3	C_2H_5O	1.06	3.61	
7	C_2H_5	C_2H_5O	1.88	3.72	
8	C_2H_5	C_3H_7O	2.00	3.81	
9	C_2H_5	C_3H_7O	2.11	3.96	

TABLE 4

Constants of the Substituents σ

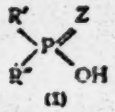
R	n	σ	$\pm\Delta\sigma$	R	n	σ	$\pm\Delta\sigma$
H	—	0	—	$m\text{-}C_5H_5N^+H_2C_6H_4$	1	+0.300	—
HO	57	−0.393	0.007	$p\text{-}NO_2C_6H_4$	4	+0.133	0.045
CH_3O	4	−0.124	0.014	$m\text{-}NO_2C_6H_4$	4	+0.096	0.041
C_2H_5O	4	−0.214	0.014	$p\text{-}NH_2SO_2C_6H_4$	4	0.000	0.030
C_3H_7O	4	−0.315	0.048	$p\text{-}HOOCC_6H_4$	2	−0.140	0.040
$i\text{-}C_3H_7O$	2	−0.291	0.004	$m\text{-}HOOCC_6H_4$	2	−0.177	0.027
C_4H_9O	3	−0.411	0.043	$m\text{-}ClC_6H_4$	4	−0.219	0.024
$i\text{-}C_4H_9O$	2	−0.300	0.000	$m\text{-}BrC_6H_4$	4	−0.229	0.028
CH_3	4	−0.965	0.023	$p\text{-}BrC_6H_4$	4	−0.248	0.015
C_2H_5	4	−1.101	0.020	$p\text{-}ClC_6H_4$	4	−0.292	0.014
C_3H_7	5	−1.177	0.025	$m\text{-}HOC_6H_4$	4	−0.322	0.022
$i\text{-}C_3H_7$	3	−0.300	0.036	$p\text{-}^-OOCC_6H_4$	2	−0.418	0.008
C_4H_9	4	−0.219	0.015	$m\text{-}^-OOCC_6H_4$	2	−0.418	0.008
$i\text{-}C_4H_9$	2	−1.297	0.010	$m\text{-}NH_2NHC_6H_4$	1	−0.485	—
sec $\text{-}C_4H_9$	2	−1.303	0.023	$p\text{-}CH_3CONHC_6H_4$	3	−0.493	0.008
tert-C_4H_9	3	−1.546	0.098	$p\text{-}C_6H_5SC_6H_4$	2	−0.500	0.045
$C_{10}H_{21}$	2	−1.309	0.031	2,4-$(CH_3O)_2C_6H_3$	2	−0.549	0.018
$ClCH_2$	2	−0.034	0.004	$m\text{-}NH_2C_6H_4$	2	−0.563	0.008
C_2ClH	2	+0.272	0.019	$p\text{-}CH_3OC_6H_4$	2	−0.586	0.004
CCl_3	2	+0.301	0.531	$p\text{-}CH_3C_6H_4$	4	−0.602	0.018
$BrCH_2$	2	−0.010	0.270	$m\text{-}C_6H_5NHC_6H_4$	1	−0.621	—
ICH_2	2	−0.111	0.211	$p\text{-}HOC_6H_4$	4	−0.653	0.017
$HOCH_2$	2	−0.548	0.030	$m\text{-}CH_3NHC_6H_4$	1	−0.654	—
CF_3	2	+0.498	0.268	$p\text{-}C_2H_5OC_6H_4$	4	−0.656	0.005
=O	—	0	—	$m\text{-}C_6H_5NHC_6H_4$	1	−0.671	—
C_6H_5	4	−0.481	0.020	$p\text{-}(CH_3)_2NC_6H_4$	1	−0.692	—
$m\text{-}CH_3N^+H_2C_6H_4$	1	+0.300	—	$p\text{-}NH_2C_6H_4$	1	−0.703	—
$p\text{-}(CH_3)_3N^+HC_6H_4$	1	+0.300	—	$p\text{-}NH_2NHC_6H_4$	1	−0.720	—
				$p\text{-}CH_3NHC_6H_4$	1	−0.841	—

TABLE 5

Constants of the Reaction ρ

Reaction	n	pK_0	ρ	±Δρ	r
Ionization of R'R"POOH acids in water; first stage	58	1.00 (1.00)	0.990 (1.000)	0.030	0.978
Ionization of R'PO(OH)$_2$ acids in water; second stage	47	6.13	1.788	0.083	0.955
Ionization of R'R"POOH acids in 50% alcohol, first stage	17	2.01	1.312	0.042	0.993
Ionization of R'PO(OH)$_2$ acids in 50% alcohol; second stage	19	7.59	1.358	0.042	0.992
Ionization of R'R"PS(OH) acids in water	9	0.31	1.203	0.069	0.989
Ionization of R'R"PS(OH) acids in 80% alcohol	9	2.65	1.272	0.070	0.990

In the present work are compared the ionization constants (pK_1 and pK_2) of organic phosphorous acids of the general formula (I) with



(I)

the ionization constants of hypophosphorous (R' = R" = H, Z = O) phosphorous (R' = H; R" = OH, Z = O) and phosphoric acid. Experimental data for acids in which R' and R" can be Alk, Aryl, AlkO, and HO, and Z, is oxygen or sulfur, which were taken from the literature and determined, in part, in the laboratory of the author, are presented in Tables 1-3.

Calculations were carried out by means of the formula

$$pK = pK_0 - \rho\Sigma\sigma, \qquad (2)$$

where pK and pK_0 are, respectively, the indices of the ionization constants of the given acid and the unsubstituted acid used as a standard. Hypophosphorous acid, H_2POOH, was used as the standard for acids of the type R'R"POOH; the anion of phosphorous acid, $^-O(H)POOH$, was used for the second stage of ionization of these acids; and for acids of the type R'R"PS(OH), the hypothetical thiohypophosphorous acid, $H_2PS(OH)$, was used. The average value of the substituent constant σ was calculated by the method of successive approximations; for these calculations, the reaction constant ρ for the first stage of ionization of the acids R'R"POOH in aqueous solution was taken as 1. For alcoholic solutions, for the constants for the second stage of ionization in water or alcohol, or for acids of the type R'R"PS(OH), the reaction constants ρ were found by the usual method, as were the values of pK_0. The average errors and the correlation coefficients (r) were found by the usual statistical treatment. The values found for σ and Δσ are presented in Table 4. The corresponding reaction constants ρ and values of pK_0 and r are presented in Table 5.

In Figures 1-3 are presented linear plots of $pK = f(\Sigma\sigma)$.

As seen from the data presented, the Hammett formula is applicable to ionization constants of phosphorus acids with good accuracy.*

Institute of Elementoorganic Compounds
Academy of Sciences, USSR

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*Only acids containing CF_3 or CCl_3 groups showed material divergence far exceeding the limits of experimental error.

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INVESTIGATION OF THE PURITY AND FREEZING POINTS OF CERTAIN ORGANIC COMPOUNDS

A. G. Anikin, Associate Member of the Academy of Sciences
Ya. I. Gerasimov, G. M. Dugacheva and N. N. Kozhevnikov

The question of the purity of substances has recently attained increased significance. That the physical and chemical properties of a given substance differ substantially from those ascribed to it earlier, when the purity of the preparations investigated was less, is explained by the degree of purity of the various classes of substances. The rather essential differences in physicochemical parameters given by different authors for one substance or another are dependent on the different nature of the impurities and the different degree of purity.

Thus, for the correct determination of the physical and chemical properties of a substance, maximum and strictly controlled degree of purity is necessary. A high degree of purity is presently achieved with inorganic compounds in many cases. The preparation of organic compounds of high purity is attended by far greater difficulties. The great similarity of physical and chemical properties of members of an homologous series, which, perhaps, finds its counterpart in the field of inorganic compounds in the similarity existing among the properties of compounds of the rare earth elements, leads to great difficulties (in principle and in practice) both in the purification and in the determination of the purity of the organic compounds. That is precisely the reason that the purity of the organic compounds, in contrast to inorganic, reaches a maximum of 10^{-3} mol % for the compounds considered; i.e., the purity of the purest individual organic compounds is lower by 3 orders of magnitude (1000 times) than that of metals.

The question of the purity of organic substances has been prominent for some time past, because component analyses of Soviet petroleum, and especially its liquid fuel fractions, have been expanded, and thermodynamic calculations on the combustion of the fuel are impossible without a knowledge of the physicochemical parameters of the individual organic compounds composing the fuel. Spectral investigations of organic compounds, which have been particularly expanded recently, also require a knowledge of the purity of organic substances (for newly synthesized substances).

The present article is a brief review of the experimental work on the determination of the purity of organic substances and the calculation of the freezing point of preparations of limited purity in the laboratory of chemical thermodynamics of the Moscow State University, where cryoscopic methods were developed based on the work of V. P. Peshkov [2] and Rossini [1]. In our method, temperature measurement is carried out by means of a thermocouple (Peshkov), and the rate of cooling or heating is regulated by means of a vacuum which is maintained between the walls of the reaction vessel (Rossini). The positive features of such a method of controlling heating are obvious. The use of a thermocouple instead of a resistance thermometer permits an appreciable reduction in the amount of material investigated. Besides the combination of these two elements of known methods, we introduced into the measuring circuit an EPP-09 electronic recording potentiometer specially remodeled for the purpose [5]. Automatic recording itself has been used for time-temperature curves during determinations of the purity of organic substances prior to our work [6-8]. The distinction of our work apparently lies in a simpler method, which formed the basis for recording and measuring temperatures [5]. The recorder registers accurately the course of the temperature of the process, thereby making it possible to carry out the investigation much more rapidly than by visual reading of a reflecting galvanometer. Moreover, the recorder permits one to tell at once, from the nature of the curve, the quality of the experiment, to record the effect of stopping the stirrer, etc. The remodeled EPP-09 has a sensitivity of 0.06°/mm; therefore, during the recording of curves in the temperature

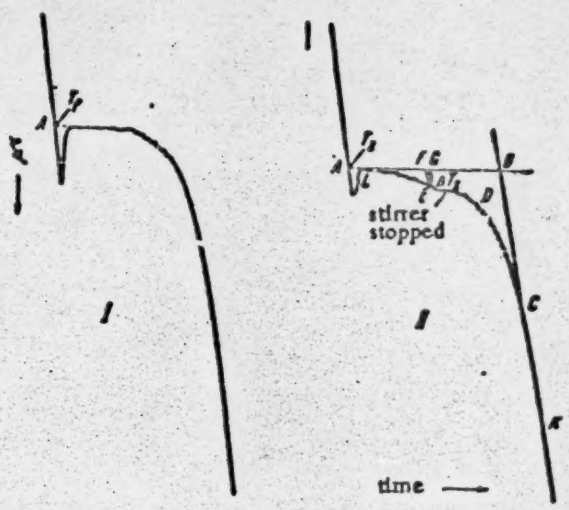

Fig. 1. Crystallization curves: I) Substance without artificial impurity; II) with artificial impurity. The construction required for determining ΔT_z was made as follows [1]: the point A (II), indicating the temperature T_z, was found by extrapolation of the equilibrium part of the curve LED. AB is a horizontal line; BC is a continuation of the part of the curve CK. Section AB was divided in half (AF = FB). From F, the line FE was constructed parallel to BC to intersect the curve; at E, GE was erected ⊥ AB. The value GE corresponds to ΔT_z.

range from 20° to zero Centigrade, it is necessary to compensate the thermal electromotive force generated by the thermocouple. For this purpose, the thermocouple was connected to the recorder through a PMS-48 potentiometer, which is apparently one of the best of the domestic low-resistance direct current potentiometers. By means of this potentiometer, accurate simultaneous measurement of the thermal emf was carried out. By varying the chart rate, rational selection of the slope of the heating and cooling curves during the processes was easily realized, the processes, as already noted, being regulated in the reaction vessel by means of the vacuum. Considerable variation in the rate of the process was also obtained by changing the temperature of the refrigerant used. The refrigerants used were dry ice and alcohol, for a temperature of −70°, and liquid nitrogen, for −190°.

The experimental apparatus consisted of a reaction cell with a thermocouple and stirrer, the vacuum apparatus, the EPP-09 electronic recording potentiometer, and the PMS-48 indicating potentiometer and its accessory equipment (standard element, adjustable current galvanometer (M/21), Z-S-T-98-VD storage battery feeding the potentiometer). All electrical apparatus was mounted on a grounded metal plate, which, to a considerable extent, eliminated stray readings.

The reaction vessel used in obtaining the crystallization curves was a double-wall vessel, the space between the walls being evacuated, with a stopcock isolating the evacuated space from the surrounding medium, and with a sleeve through which the vessel was joined to the vacuum apparatus. The vessel was provided with a nichrome stirrer and a copper-constantan thermocouple mounted in the stopper [4] (this couple gave most stable readings during the work in low temperature regions). The stopper had an opening for a cooling needle. The vessel had an internal diameter of approximately 17 mm and a length of 270-300 mm. 10-12 ml of the substance being investigated was used. The amount of impurities was determined with an accuracy of about 10% of the total amount. This determined the accuracy of the freezing point determinations. All substances analyzed by us up to the present have had from 1 to 5 mol.% impurities; the absolute accuracy of the determination of the per cent impurities was ±0.1%, in accordance with which the absolute accuracy of the freezing point determinations was ±0.1°.

The use of automatic recording of the crystallization curves (time-temperature curves) introduces, to our way of thinking, an essential improvement into the method of the investigations. Automatic recording of the curves: 1) is more objective than that used in existing methods, subjective recording to the position of the indicating line of light of the galvanometer; 2) it frees the experimenter from routine work; 3) it registers details of the curve which can be passed over, for example, in the method of Rossini, where the interval between neighboring points on the curve is 2-3 minutes; this is particularly essential for substances exhibiting considerable supercooling, after which the curve proceeds almost vertically upward (heating) and it is important to catch the highest temperature on the curve after the supercooling (in visual investigations, the peak of the curve can sometimes fall between two observations); 4) automatic inking of the crystallization curves gives a real curve at the time of the experiment, and not afterwards as in other methods; this economizes on time, since it permits stopping in the middle or even at the beginning of an unsuccessful experiment.

It should be noted that the indicating potentiometer (which compensates part of the thermal emf) was installed before the recorder. Any movement of the control arm of the potentiometer during the recording distorted the curve.

The thermocouple was standardized against a standard platinum resistance thermometer. As a constant temperature medium, we used any substance whose freezing point satisfied the following requirements: 1) comparatively high heat of crystallization; 2) a crystallization temperature in the lower interval; 3) a sufficiently high degree of purity (> 97%) that the plateau on the cooling curve was horizontal.

The role played by stirring of the substance during the experiment should be especially emphasized. During an experiment, the substance was always stirred by means of a mechanical stirrer. Stirring is required for an approach to thermodynamic equilibrium and, consequently, for the determination of the equilibrium freezing point. Thus, for example, in experiments on the determination of the freezing point of dichloroethane in which the stirrer was shut down, the average error was $\pm 15\mu v$ which amounted to $\pm 0.6°$ in that temperature interval. In work with the stirrer, scattering of the measurements was decreased to $\pm 1\ \mu v$ or 0.05°.

The stirrer was constructed of nichrome wire 1.5-2 mm in diameter, and had several loops at the end. The motor-driven stirrer moved up and down a distance of 5 cm at a rate of 85-120 movements per minute.

If the substance crystallized with considerable supercooling, thereby distorting the experimental results, a nichrome wire cooling needle, the end of which was pre-cooled in liquid nitrogen, was used.

The following assumptions [1] were made in evaluating the amount of impurities: 1) constant rate of crystallization of the substance; 2) liquid and crystalline phases in thermodynamic equilibrium; 3) the impurities remain in the liquid phase to the end of the period in which the freezing point lowering was determined; 4) the impurities were present in quantities such that the solution was sufficiently dilute to obey Raoult's law (up to 6 mol. % impurities).

The crystallization temperature of the initial substance was taken as the point of beginning of the plateau, if supercooling was absent, and, in the event of supercooling, as the point of intersection of the extrapolated equilibrium curve with the cooling curve, the curve being extrapolated in the interval prior to supercooling (Figure 1, Point A). The freezing point of the initial material was considered to be determined when the results of 3-5 repetitive experiments agreed within about 0.1°. Afterwards, a series of curves was obtained for the substance after the addition of artificial impurity (2-4 mol.%) required for calculation of the cryoscopic constant and the degree of purity (Figure 1).

The freezing point, T_z, of the substance with artificial impurity [N] was lower than the freezing point of the initial sample, T_f, by an amount ΔT_f and the equilibrium part of the curve (the plateau) was steeper. Calculation of the purity and of the freezing point of the absolutely pure substance was carried out as follows [1]:

1. The cryoscopic constant, A, was calculated from [3]:

$$A = \frac{N\left(1 + \frac{1}{2}N\right)}{T\Delta_f}. \qquad (1)$$

2. The amount of natural impurity, N°, was determined from the equation:

$$N^{\circ} = \frac{1-r}{2-r}\left[-1+\sqrt{1+2A\left(\frac{2-r}{r}\right)\Delta T_s}\right]. \quad (2)$$

where r indicates the part of the substance (with artificial impurity) frozen at a given time, ΔT_s is the difference between the freezing point of the sample with artificial impurity added and the freezing point of the same sample at r, which is conveniently taken as 1/2 ΔT_z determined graphically.

3. The freezing point of the absolutely pure substance, T_{f0}, was calculated from the equation [1]:

$$T_{f_0} = \frac{N^{\circ}\left(1+\frac{1}{2}N^{\circ}\right)+AT_f}{A}. \quad (3)$$

A detailed derivation of these equations is given in the cited work of Rossini [2].

EXPERIMENTAL DATA

The method described was used to investigate the following substances: 1,4-diisopropylbenzene, 1,1-diethylcyclopentane, isooctane, dicyclopentyl, and 1-butyl-1-cyclopentene in amounts of 10-15 ml (the materials were synthesized in the laboratory of Prof. R. Ya. Levina (MSU), in the laboratory of Prof. A. F. Plate (MSU), and in the laboratory of A. L. Liberman of the Institute of Organic Chemistry).

TABLE 1

Sample	Artificial impurity	F. p. of the initial sample, °C	F. p. of the absolutely pure substance, °C	Amount of impurity, mole fraction
1,4-Diisopropylbenzene	p-Xylene	− 17.2	− 16.9	0.010
1,1-Diethylcyclopentane	Methylcyclohexane	−107.1	−106.4	0.041
Isooctane	Methylcyclohexane	−108.05	−107.5	0.026
1-Butyl-1-cyclopentene	1-Butylcyclopentane	− 88.35	− 87.9	0.025
Dicyclopentyl	Toluene	− 35.7	− 35.1	0.020

Freezing and melting curves were made for the indicated initial substances with and without artificial impurity (the impurity was used in the amount of 2-4 mol.%). The freezing point of the absolutely pure substance without added impurity and the purity of the initial sample were calculated for each substance (Table 1).

M. V. Lomonosov Moscow State University

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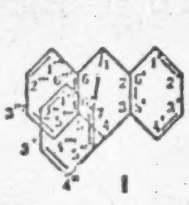
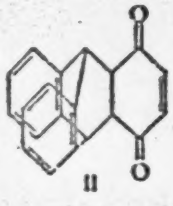
CATALYTIC HYDROGENATION OF TRIPTYCENE DERIVATIVES

Academician A. A. Balandin and E. I. Klabunovsky

The study of the catalysis of molecules of complex structure, which are disposed with difficulty on the surface of the catalyst, is of great interest from the point of view of multiplet theory [1]. With this aim, we conducted experiments on the hydrogenation of triptycene (I) [(2,3;5',6') (5,6;5",6") (7,8;5"',6"')-tribenzobicyclo-(2,2,2)-octatriene-2,5,7] derivatives: 1,4,5,6-tetrahydro-(2,3;5',6') (5,6;5",6") (7,8;5"',6"')-tribenzobicyclo-(2,2,2,)-octadiene-5,7-dione-1',4' (II) and triptycenequinone (III) [1,4-dihydro-(2,3;5',6') (5,6;5",6") (7,8;5"', 6"')-tribenzobicyclo-(2,2,2)-octatriene-2,5,7-dione-1',4'].



I



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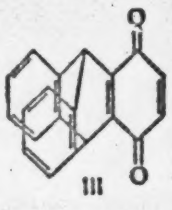
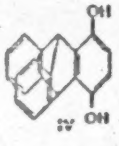
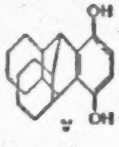


III

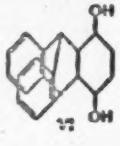
The synthesis and certain transformations of triptycene derivatives have been described in the works of Kremann [2] and Bartlett et al [3, 4]. It was shown that (II) is isomerized by the action of 40% HBr into triptycene-hydroquinone [(2,3;5',6') (5,6;5",6") (7,8;5"',6"')-tribenzobicyclo-(2,2,2)-octatriene-2,5,7-diol-1',4'] (IV). Reduction of (IV) in dioxane solution over a skeletal nickel catalyst at 83 atm and 200° leads to 1",2",3",4",5", 6",1"',2"',3"',4"',5"',6"'-dodecahydro-(2,3;5',6') (5,6;5",6") (7,8;5"',6"')-tribenzobicyclo-(2,2,2)-octene-2-diol-1', 4' (V). The use of copper chromite as the catalyst in the hydrogenation of (II) in dioxane solution at 160° and elevated pressure (160 atm) is accompanied by hydrogenation of the hydroxyl-containing ring with the formation of (1',2',3',4',5',6')-hexahydro-(2,3;5',6') (5,6;5",6") (7,8;5"',6"')-tribenzobicyclo-(2,2,2)-octadiene-5,7-diol-1', 4' (VI).



IV



V



VI

In contrast to the above work where compound IV was reduced at elevated pressure, we carried out the reduction of compounds II and III at atmospheric pressure using a skeletal nickel catalyst, and investigated the reaction rate.

The synthesis of compound II was carried out as described in the literature [3]. The original anthracene was recrystallized from toluene (m.p. 217°); the benzoquinone was purified by recrystallization and sublimation (m.p. 115°). The product of the condensation of anthracene with benzoquinone – compound II – was washed with water to remove quinhydrone and recrystallized from toluene. The yield was 62% of theoretical.

Found %: C 83.99; 84.01; H 4.85; 4.94. $C_{22}H_{14}O_2$. Calculated %: C 83.91; H 4.69.

A previously described phenomenon was observed on heating II: a yellowing at 207°, the appearance of a red color at 210°, and charring at a higher temperature.

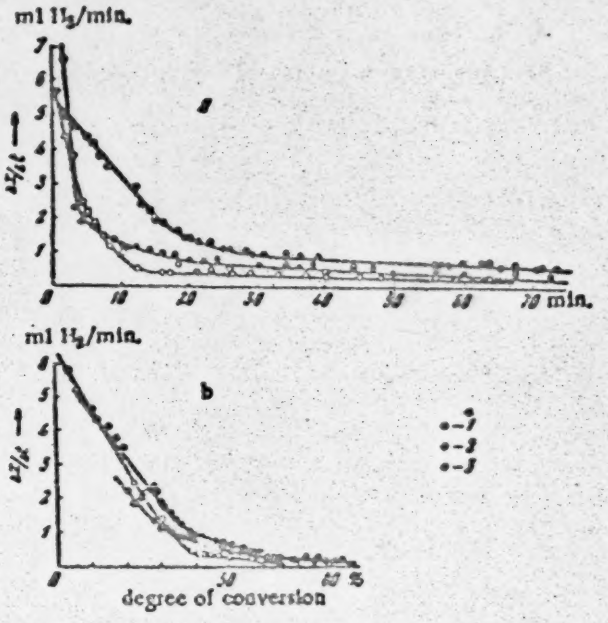


Fig. 1. Dependence of the rate of hydrogenation $\Delta x/\Delta t$, ml H_2 (STP) per minute, of compound II on: a) time t (minutes); b) degree of conversion $\frac{\Sigma x}{2}\frac{1}{V_0} \cdot 100(\%)$. 1) 0.7344 g II, V_0 = 172.6 ml H_2, 0.5 g Ni; 2) 0.4484 g II, V_0 = 105.4 ml H_2, 0.35 g Ni; 3) 0.2814 g II, V_0 = 66.2 ml H_2, 0.35 g Ni

The hydrogenation of II was carried out in a rocking bomb (250 oscillations per minute) in a toluene or dioxane medium at 45° and atmospheric pressure over a skeletal nickel catalyst prepared by the usual method. The hydrogen was obtained by the electrolysis of 30% KOH, purified from traces of oxygen over reduced copper, and dried over H_2SO_4. Control experiments showed that the solvent did not absorb hydrogen under these conditions. Prior to introduction of the sample of starting material into the bomb, the catalyst was agitated in an atmosphere of hydrogen until saturated.

The hydrogenation product, recrystallized from dioxane, was in the form of colorless crystals, m.p. 224-227° (with decomposition). The pure product was not oxidized in air in the presence of alkali.

Found %: C 82.10; 82.12; H 6.93; 6.98. $C_{22}H_{22}O_2$. Calculated %: C 82.15; H 6.90.

The course of the hydrogenation in the individual experiments is presented in figure 1 in which the coordinates are H_2-absorption rate – time, and rate – degree of conversion in %. Three moles of hydrogen were absorbed in the hydrogenation, which leads to the formation of the diol VI. The break in the curves corresponds to the absorption of 1 mole of hydrogen.

Compound II underwent isomerization under the influence of 40% HBr [3] in boiling glacial acetic acid yielding triptycenehydroquinone IV in 75% yield. After recrystallization from a mixture of toluene and dioxane

(7 : 1), the product melted at 328° (decomposed at 336-342°). Triptycenehydroquinone is oxidized to III by a 1% aqueous solution of $KBrO_3$ in boiling glacial acetic acid [3]. Triptycenequinone was obtained with a yield of 70% after recrystallization from toluene, it melted at 292° (with decomposition).

Found %: C 84.24; 84.27; H 4.19; 4.20. $C_{20}H_{12}O_2$. Calculated %: C 84.50; H 4.23.

The dioxime melted at 245-247° (with decomposition).

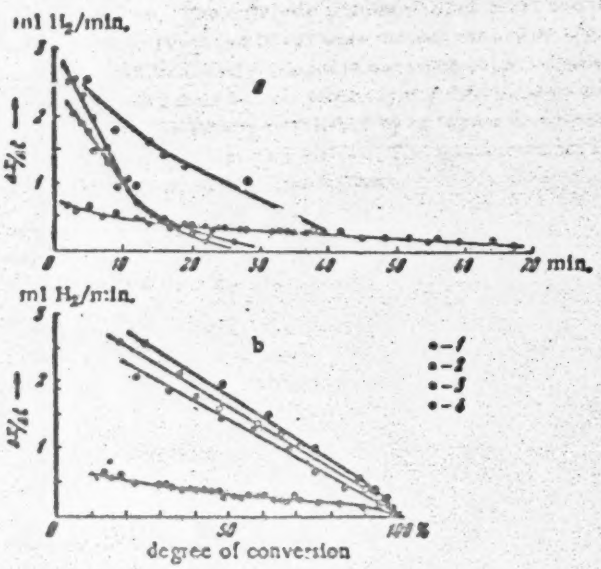


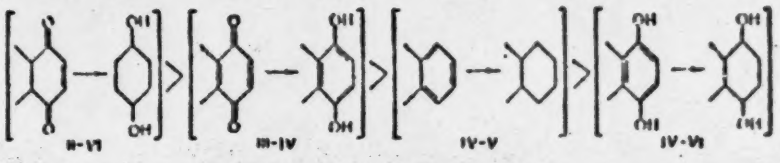
Fig. 2. Dependence of hydrogenation rate $\Delta x/\Delta t$, ml H_2(STP) per minute, on: a) time t (min.); b) degree of conversion $\frac{\Sigma x}{2}\frac{1}{V_0} \cdot 100$ (%) of triptycenequinone (1, 2, and 3) and cinnamic acid (4). 1) 0.2724 g, V_0 = 21.7 ml H_2, 0.35 g Ni; 2) 0.3037 g, V_0 = 24.0 ml H_2, 0.35 g Ni; 3) 0.6316 g, V_0 = 47.8 ml H_2, 0.50 g Ni; 4) 0.2006 g, V_0 = 30.3 ml H_2, 0.35 g Ni.

Triptycenequinone, III, was subjected to catalytic hydrogenation over skeletal nickel catalyst at 45° and atmospheric pressure in a medium of freshly distilled dioxane (reaction in the absence of peroxides). 1 mole of hydrogen was consumed in the reaction, which leads to the formation of triptycenehydroquinone, IV. The product, after repeated recrystallization from a mixture of toluene and dioxane (7 : 1), melted at 338° (with decomposition). A mixed melting point determination gave no depression.

Found %: C 83.54; 83.60; H 4.96; 5.02. $C_{20}H_{14}O_2$. Calculated %: C 83.91; H 4.89

The course of the hydrogenation of III at 45° is seen in Figure 2. Curve 4 of the hydrogenation of cinnamic acid under the same conditions is presented for comparison. Data similar to those presented in Figures 1 and 2 were obtained at 25°. The total amount of hydrogen absorbed in all of the work was close to the theoretical amount (V_0).

Thus, the following catalytic hydrogenations are now experimentally known for triptycene derivatives.



In the scheme are presented only the reacting parts of the molecules of triptycene derivatives, the formulas of which were presented above. The catalytic transformations II-VI and III-IV were carried out in the present work, and the transformations IV-V and IV-VI were carried out earlier [3]; the latter reaction did not go over nickel under the stated conditions, and was carried out using copper chromite as the catalyst. The reactions on the left of the > sign proceeded over nickel more rapidly than those on the right. The comparative ease of the transformations II-VI and III-IV was established by us from a comparison of the rates of reactions carried out under the same conditions (cf. Figures 1 and 2). The transformations II-VI and III-IV undoubtedly consist of several steps. The latter must be clarified further.

The series of reactions of the above scheme develops experimentally the series of hydrogenation reactions over nickel derived from the multiplet theory [5].

Let us consider a model of the active catalytic complex formed during the transformation IV-V.

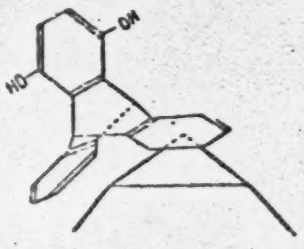


Fig. 3. Model of the hydrogenation of benzene rings of triptycenehydroquinone on the (111) face of nickel crystals.

According to the multiplet theory, during hydrogenation over nickel the benzene rings lay flat on the catalyst surface, and this is confirmed by a series of experimental facts [1]. The course of the hydrogenation of benzene rings in a molecule of such complex three-dimensional structure as triptycene in the transformation IV-V indicates that on the surface of the catalyst, together with the projecting active centers on which the hydrogenation of the benzene rings takes place, there are rather large troughs where the other benzene rings of the molecule are disposed. Successive hydrogenation of benzene rings can proceed on the (111) faces, which cut the (100) face of the nickel crystals (see Figure 3).

Similar conclusions on the distribution of active centers on projecting surfaces of the catalyst were formed during a study of the catalytic dehydrogenation of unsymmetrical diphenylethane, where the reaction takes place not in the nucleus, but, on the contrary, in the side chain [6]. There the side chain is superimposed on the surface projection, and the benzene nuclei are disposed one outwards and the other in the trough.

The stereochemistry of the activated complexes in reactions of other triptycene derivatives will be considered separately.

N. D. Zelinsky Institute of Organic Chemistry
Academy of Sciences, USSR

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STEREOCHEMISTRY OF SYMMETRIZATION REACTIONS OF 3-BROMOMERCURICAMPHOR

O. A. Reutov and Lu Tszin-Chzhu

(Presented by Academician A. N. Nesmeyanov, April 25, 1956)

Symmetrization of organomercury compounds proceeds both under the influence of complex formers, which attack the halomercuri group (KI, KCN, KCNS, $Na_2S_2O_3$, NH_3), and under the influence of reducing agents (hydrazine hydrate, sodium stannite).

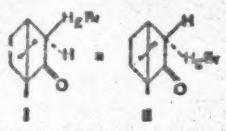
$$2R-HgX \rightarrow R-Hg-R$$

As was shown by A. N. Nesmeyanov, S. S. Poddubnaya and one of us [1], symmetrization of diastereoisomeric l-methyl esters of d- and l-α-bromomercuriphenylacetic acids under the influence of ammonia is an electrophilic substitution reaction at a saturated carbon atom and proceeds with preservation of the configuration.

In the present work are reported the results of a study of the stereochemistry of the symmetrization of organomercuri derivatives of camphor under the influence of sodium hyposulfite [thiosulfate] and hydrazine hydrate.

The mixture of diastereoisomers of 3-bromomercuricamphor, m.p. 218-220° and $[\alpha]_D^{18}$ −74.4°, was prepared by mercurization of l-camphor [2].

The diastereoisomers, which differ in the configuration of the α-carbon atom,

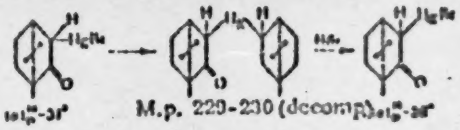


I II

have the following constants: I — m.p. 222-223°, $[\alpha]_D^{18}$ −30.7°; II — m.p. 216-218°, $[\alpha]_D^{18}$ −126°. Diastereoisomer I was easily isolated in the pure form, since it is less soluble and more stable.

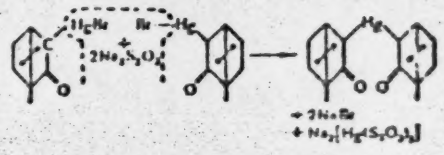
Symmetrization of diastereoisomer I and 3-bromomercuricamphor by sodium hyposulfite in aqueous solution leads chiefly to the formation of a single isomer of mercuri-bis-camphor [dicamphorylmercury] (with a small amount of the second stereoisomer). This is apparent from the fact that the reaction of the symmetrical product with an equimolar amount of alcoholic hydrogen bromide yields almost pure diastereoisomer I of 3-bromomercuricamphor. •

• The admixture of the second isomer of mercury-bis-camphor probably indicates that, simultaneously with the symmetrization reaction, there occurs an extremely slow racemization of the configuration of the α-carbon atom of the original diastereoisomer of 3-bromomercuricamphor under the influence of hydroxyl ions.



M.p. 229-230 (decomp.)

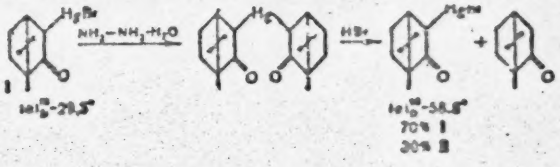
It follows from these results that the configuration of the α-carbon atoms of both reacting molecules of 3-bromomercuricamphor is preserved during the symmetrization reaction. Thus, symmetrization of organomercury salts by sodium hyposulfite is an electrophilic substitution at a saturated carbon atom and proceeds with preservation of the configuration.



Apparently, symmetrization of organomercury compounds is an electrophilic substitution reaction which proceeds with preservation of the configuration at the saturated carbon atom, not only in the case of hyposulfite and ammonia [1], but also in the case of other complex formers, which attack the halomercuri group (KI, KCN, KCNS).

With the use of reducing agents, such as hydrazine hydrate or sodium stannite, as the symmetrizing agent, it would be expected that the symmetrization reaction, which is accompanied by the liberation of metallic mercury, would take place by a homolytic, not a heterolytic, mechanism.

Symmetrization of diastereoisomer I of 3-bromomercuricamphor, $[\alpha]_D^{18}$ −29.5°, by hydrazine hydrate leads to the formation of a mixture of two diastereoisomers of mercuri-bis-camphor. The action of an equimolar amount of alcoholic hydrogen bromide on this mixture of diastereoisomers yields a mixture of 3-bromomercuricamphor diastereoisomers which has an m.p. of 220-222° and $[\alpha]_D^{18}$ −58.8° after recrystallization from aqueous dioxane.* It is apparent from the value of the angle of rotation that the mixture consisted of 70% diastereoisomer I ($[\alpha]_D^{18}$ −30°) and 30% diastereoisomer II ($[\alpha]_D^{18}$ −120°).



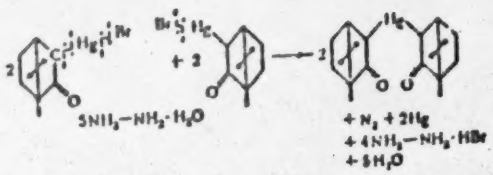
It follows from these results that, during the symmetrization reaction, the configuration at the α-carbon atom of one of the molecules of organomercury salt is preserved, and the configuration at the α-carbon atom of the other molecule (which is acted on during the reaction) racemizes. Thus, symmetrization by means of hydrazine hydrate is a substitution reaction proceeding with racemization of the configuration of the carbon atom at which the substitution takes place.**

* Prior to recrystallization (after washing the camphor with alcohol, the mixture of diastereoisomers had $[\alpha]_D^{18}$ −65.8°.

** When an insufficient amount of hydrazine hydrate is used in the reaction with diastereoisomer I of 3-bromomercuricamphor, the unreacted 3-bromomercuricamphor is almost pure diastereoisomer I ($[\alpha]_D^{18}$ −39°. From this fact, it follows that racemization of the configuration at the α-carbon atom under the influence of hydrazine hydrate — a basic reagent — under our conditions is not appreciably significant and cannot alter our results.

On the other hand, during work with the unstable diastereoisomer II, we observed that it was rapidly converted by the action of hydrazine hydrate into diastereoisomer I. Thus, with the action of an insufficient amount of hydrazine hydrate on diastereoisomer II, the unreacted 3-bromomercuricamphor was an approximately equimolar mixture of diastereoisomers I and II ($[\alpha]_D^{18}$ −73°). In this connection, it is clear why symmetrization of diastereoisomer II led to the same mixture of isomers of mercuri-bis-camphor as was obtained by symmetrization of diastereoisomer I.

Thus, that symmetrization reaction which is an electrophilic substitution process takes place with preservation of the configuration; the occurrence of racemization during symmetrization with hydrazine hydrate indicates the radical nature of this reaction.



It was not possible to carry out the symmetrization of 3-bromomercuricamphor with sodium stannite (only camphor was formed); however, under conditions where this reaction is possible, there is reason to assume that it will proceed with racemization of the configuration of the carbon atom at which the substitution takes place.

M. V. Lomonosov Moscow State University

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* T. p. = C. B. Translation pagination

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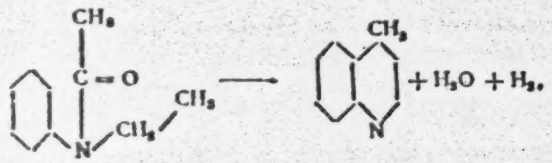
LEPIDINE REARRANGEMENT OF ETHYLACETANILIDES

B.I. Ardashov

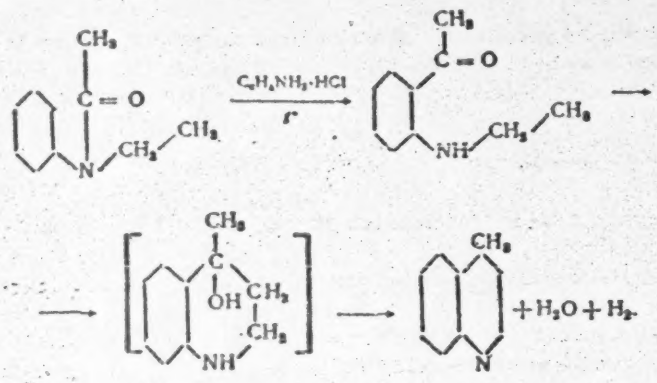
(Presented by Academician I.N. Nazarov, May 5, 1956)

In 1889, Pictet and Bunzl [1] carried out a condensation of ethylacetanilide in the presence of zinc chloride expecting to obtain lepidine according to



but, instead, they obtained quinaldine. In 1952, we showed that this reaction yields only α- and β-quinolines [2].

We have now established that this reaction yields lepidine when carried out in the presence of aromatic amine hydrochlorides (aniline and its homologs, diphenylamine, etc.). Homologs of aniline form homologs of lepidine; thus para-toluidine yields 4,6-dimethylquinoline. There is basis for the conclusion that the aromatic amine ties up the migrating ethyl radical, which displaces the mobile hydrogen of the amino group, and thus, instead of o-ethylacetanilide, the intermediate product in the formation of quinaldine, o-ethylaminoacetophenone is formed and cyclizes to lepidine.



In this reaction, the catalytic effect of aromatic amines on the process of cyclization of ethylacylanilides, observed in other quinoline synthesis reactions [3], is uniquely exhibited. Although in this reaction the yields of lepidine bases are 2-3 times higher* than are the yields of quinaldines in the Pictet reaction [1], they comprise only about 20% of the raw base even in an improved variant. It can be assumed that aliphatic amines behave similarly in natural processes, for example in the formation of alkaloids in plants, where the synthesis

*According to [3], it is necessary here to take into account the intermediate formation of dianil.

reaction takes place under mild conditions. It appears to us that aromatic amines can be used similarly in other cases of radical rearrangements, for example with the aim of establishing the mechanism of radical rearrangements.

In the future, we intend to apply the "lepidine" rearrangement, established by us, to the synthesis of various lepidine bases and also to investigate the effect of amines in other radical rearrangements.

EXPERIMENTAL

Preparation of lepidine. Experiment 1. A mixture of 16.3 g of ethylacetanilide, 16.3 g of freshly fused zinc chloride, and 13 g of aniline hydrochloride was heated on an oil bath at 300-310°* for 4 hours. The melt was dissolved in boiling hydrochloric acid (1:3), (on occasion, it was immediately treated with alkali), alkalized with a 40% solution of sodium hydroxide, and the base steam distilled. The quinoline base was purified by means of potassium ferrocyanide [4,5]. 1.4 g (10%) of a fraction boiling at 235-265° was obtained by distillation. If the ethylacetanilide is added portion-wise, 2-3 minutes per portion, over the course of 1.5-2 hours, allowing the temperature to rise to 290°, the yield of lepidine is increased to 17-20%.** M.p. of the picrate, prepared in alcohol, was 205°; after recrystallization from alcohol, it was 211-212°. A mixed melting point with a known sample of lepidine picrate showed no depression. The chloroplatinate melted at 235°, the chloroaurate at 186° with decomposition. Oxidation of the base gave cinchoninic acid.

Oxidation of the base [6,7]. 5 g of lepidine and 7.5 g of 40% formaldehyde were sealed in an ampoule and heated on a water bath for 48 hours. 9.9 g of the methylol derivative of lepidine was obtained. The latter was dissolved in 112 ml of concentrated nitric acid and heated for 20 hours. The rest of the process was carried out as described in [7].

The raw cinchoninic acid melted at 241°; recrystallization yielded 0.12 g of cinchoninic acid melting at 252-253° (20%).

5.65 ml of 0.1 N NaOH titrated 0.1 g of the substance. The calculated amount of 0.1 N NaOH is 5.8 ml.

Analysis of the picrate of the base:

Found %: N 15.23. $C_{10}H_9NC_6H_2(NO_2)_3OH$. Calculated %: N 15.05.

Preparation of 4,6-dimethylquinoline. Experiment 2. 17.7 g of ethylacetparatoluidine [p-ethylacetotoluide], 16.3 zinc chloride, and 13 g of aniline hydrochloride were used. The experiment was carried out similarly to the first experiment.

The yield of the 235-270° fraction was 2.2 g (14%). The yield of 4,6-dimethylquinoline was increased to 20-22% by adding the ethylacettoluide dropwise over a period of 2 hours. The picrate melted at 223°; after recrystallization from alcohol, it melted at 237°. A mixed melting point with a known sample of 4,6-dimethylquinoline picrate showed no depression.

Nitrogen analysis: 0.1 g of material gave 13 ml of N_2 (21°, 754 mm).

Found %: N 14.61. $C_{11}H_{11}NC_6H_2(NO_2)_3OH$. Calculated %: N 14.51.

Preparation of lepidine from orthoethylaminoacetophenone. Experiment 3. A mixture of 16.3 g of o-ethylaminoacetophenone and 16.3 g of zinc chloride were heated on an oil bath at 300-310° for 4 hours. Isolation of the base was carried out similarly to the first experiment. About 0.5 g (4%) of a fraction boiling at 235-265° was obtained. M.p. of the picrate was 207°, 211° after recrystallization from alcohol. A mixed melting point with a sample of known lepidine picrate showed no depression.

M.A. Mostoslavsky and A.A. Tofanovskaya took part in the experimental work.

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V.M. Molotov Rostov State University

*Cyclization does not occur at a temperature below 290°.

**The addition of 5 g of anhydrous ferric chloride increases the yield somewhat.

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SULFONATION OF β-DIKETONES WITH DIOXANE-SULFUR TRIOXIDE

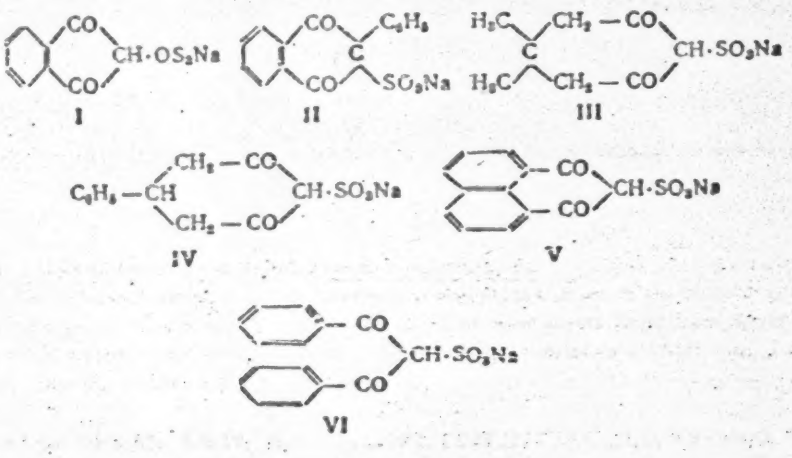
E.Yu. Gudrinietse, E.Ya. Dreimanis and G.Ya. Vanag

(Presented by Academician I.N. Nazarov, May 5, 1956)

Dioxane-sulfur trioxide (D-SO_3) has been successfully used for the sulfonation of many organic compounds which are difficultly sulfonatable by the usual method, for example, many heterocyclic compounds, aldehydes, ketones, dienes, etc. [1]. There are no data in the literature on the sulfonation of β-diketones. V.N. Ufimtsev [2] described 1,3-indandione-2-sulfonic acid (1,3-diketohydrindine-2-sulfonic acid), the potassium salt of which he obtained from 2-methyl-1,4-naphthoquinone-3-sulfonic acid. Since β-diketones are studied in our laboratory, particularly their nitration and nitration products [3,4], the corresponding sulfo compounds were of interest to us.

1,3-Indandione-2-sulfonic acid, which was isolated in the form of the sodium salt (I), was prepared by sulfonation of 1,3-indandione with dioxane-sulfur trioxide. The sulfonation was carried out in 1,2-dichloroethane solution at room temperature. The reaction goes in carbon tetrachloride solution, but more difficultly, probably owing to the lower solubility of 1,3-indandione. The sulfonic acid obtained was dissolved in water and salted out with sodium chloride. The potassium salt was precipitated from a solution of 1,3-indandione-2-sulfonic acid by salting out with potassium chloride. It dissolved in water giving a yellow color in contrast to the potassium salt prepared by V.N. Ufimtsev. The yellow color disappeared on acidification. It is not impossible that this was a derivative of the enol form, a possibility which is subject to further clarification.

The sulfonation was also carried out on some other β-diketones at our disposal, namely, 2-phenyl-1,3-indandione, dimedon, 5-phenylcyclohexane-1,3-dione, 1,3-perinaphthindandione, and dibenzoylmethane. It was shown that all of these compounds are easily sulfonated by D-SO_3 at ordinary temperature in 1,2-dichloroethane solution, and only perinaphthindandione was more easily sulfonated in carbon tetrachloride solution by heating for 10 minutes. The corresponding sodium salts (II-VI) were isolated by salting out the solutions of the sulfonic acids. Yields reached 70-80%. Thus, here is a new, convenient method for introducing the sulfonic acid group into the active methylene group of β-diketones.

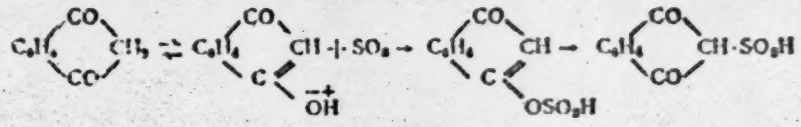


I II III

IV V

VI

The reaction mechanism is apparently the same as in the sulfonation of aldehydes and ketones. The opinion has been expressed in the literature [5] that the sulfonation proceeds through the enol form of aldehydes and ketones. Since β-diketones frequently react in their enol form, the following reaction mechanism is possible:



The salts of these sulfonic acids are stable and easily soluble in water. The sulfonic acids themselves were not isolated in the completely pure form.

EXPERIMENTAL

1,3-Indandione-2-sulfonic acid

Sodium salt. To a suspension of 6 g of D–SO_3 (0.025 mole) in 50 ml of 1,2-dichloroethane was added, with vigorous stirring, 7.3 g (0.05 mole) of 1,3-indandione, the temperature not being permitted to rise above 25°. A homogeneous, red solution was formed, and, after 2-3 minutes, the entire mass thickened. It was permitted to stand at room temperature for 1.5 hours with occasional stirring. It was then diluted with 50 ml of water, agitated well, and the aqueous solution of sulfonic acid separated from the 1,2-dichloroethane in a separatory funnel. The latter was washed 1-2 times with 30-40 ml of water. The combined aqueous solutions were saturated with sodium chloride. The sodium salt of 1,3-indandione-2-sulfonic acid (I) precipitated in the form of yellow crystals. After crystallization from dilute ethanol (15 ml of ethanol + 30 ml of water), 9.8 g (69%) of the pure product was obtained. The salt crystallized with two molecules of water which were eliminated at 100°, whereupon the crystals disintegrated into powder. The salt was easily soluble in water giving a yellow solution; it was insoluble in organic solvents.

Found %: Na 8.01; S 11.40; H_2O 13.15. $C_9H_5O_5SNa \cdot 2H_2O$. Calculated %: Na 8.09; S 11.28; H_2O 12.67.

Potassium salt. This salt was obtained by saturation of an aqueous solution of the sulfonic acid with potassium chloride. The colorless prisms did not contain water of crystallization. It was less soluble in water than the sodium salt; 3.5 g could be recrystallized from 115 ml of water. The aqueous solution was yellow, the color disappearing upon acidification.

Found %: K 14.70; S 11.65; 12.35. $C_9H_5O_5SK$. Calculated %: K 14.79; S 12.12.

Ammonium salt. This salt was prepared similarly to the sodium and potassium salts by salting out with ammonium chloride. It was easily soluble in water, imparting a yellow color.

Found %: N 5.54. $C_9H_5O_5SNH_4$. Calculated %: N 5.74.

Diethylamine salt. This salt was prepared similarly to the preceding. It was easily soluble in water.

Found %: N 4.86. $C_{13}H_{15}O_5N$. Calculated %: N 4.71.

Sodium salt of 2-phenyl-1,3-indandione-2-sulfonic acid (II). This compound was prepared by sulfonation of 2-phenyl-1,3-indandione similarly to indandione and precipitation of the sodium salt with sodium chloride. The colorless crystals were easily soluble in water. They were crystallized from dilute alcohol (25 ml of ethanol + 10 ml of water). The salt contained 3 molecules of water of crystallization. 2 molecules were eliminated at 100°, the third only at 120°.

Found %: Na 5.87; S 8.47; H_2O 9.44 (100°); 14.21 (120°). $C_{15}H_9O_5SNa \cdot 3H_2O$. Calculated %: Na 6.08; S 8.46; H_2O 9.54 (100°); 14.29 (120°).

Sodium salt of 5,5-dimethyl-1,3-cyclohexanedione-2-sulfonic acid (III). This compound was prepared by sulfonation of 5,5-dimethyl-1,3-cyclohexanedione (dimedon) similarly to the preceding, and isolation of the sodium salt by salting out with sodium chloride. The long, prismatic crystals contained 2 molecules of water. The salt was recrystallized from 50% alcohol.

Found %: Na 8.18; S 11.52; H_2O 13.23. $C_8H_{11}O_5SNa \cdot 2H_2O$. Calculated %: Na 8.27; S 11.52; H_2O 12.91.

Sodium salt of 5-phenyl-1,3-cyclohexanedione-2-sulfonic acid (IV). This compound was prepared similarly to the preceding. It was less soluble in water than the sodium salt of dimedonsulfonic acid; 17.5 g of the sodium salt could be recrystallized from 200 ml of water.

Found %: Na 7.90; S 11.23. $C_{12}H_{11}O_5SNa$. Calculated %: Na 7.92; S 11.01.

Sodium salt of 1,3-perinaphthoindandione-2-sulfonic acid (V). 1.96 g (0.01 mole) of 1,3-perinaphthoindandione, 2.5 g (0.01 mole) of D – SO_3, and 100 ml of carbon tetrachloride were refluxed for 10 minutes. The resulting perinaphthindandionesulfonic acid was filtered, dissolved in water, and salted out with sodium chloride. The resulting sodium salt was recrystallized from 50% alcohol. The yield was 2.60 g (87%) of the pure product.

Found %: Na 7.91; S 10.60. $C_{13}H_7O_5SNa$. Calculated %: Na 7.71; S 10.76.

Sodium salt of dibenzoylmethanesulfonic acid (VI). This compound was prepared by sulfonation of dibenzoylmethane in dichloroethane. Upon saturation of the sulfonic acid solution with sodium chloride, an oily product, which soon solidified, initially separated. It was recrystallized from dilute alcohol (2 parts alcohol + 1 part water). It was easily soluble in water. It crystallized with one molecule of water.

Found %: Na 6.65; S 8.79; H_2O 4.69. $C_{15}H_{11}O_5SNa \cdot H_2O$. Calculated %: Na 6.69; S 9.31; H_2O 5.24.

Our appreciation is expressed to Prof. Doctor of Chemical Science A.F. Ievinsh for council and aid on the analytical part of the work.

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Latvian State University

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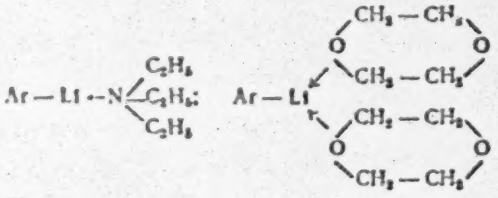
COMPLEXES OF ALKYLLITHIUM AND DIALKYL SULFIDES

B.A. Dolgoplosk, V.A. Kropachev and N.I. Mikolaev

(Presented by Academician I.N. Nazarev, May 5, 1956)

In the series of organometallic compounds, the phenomenon of complex formation is well known for the organomagnesium derivatives [1,2]. Certain of the products of the addition of ethers and amines to compounds of the type RMgX have been isolated in the crystalline state, and their compositions have been established [3, 4]. As substances forming complexes with compounds of the type RMgX, the following may be noted: ethers [1], amines [2], dioxane [5], tribenzylphosphine oxide [6], etc.

Up to the present, a series of works have appeared in which the ability of organic compounds of the alkali metals to form various complexes has been recorded. Two complexes of triphenylmethyllithium are known, an ammoniate, $(C_6H_5)_3CLi \cdot NH_3$ [7], and a complex with two molecules of ether [8], $(C_6H_5)_3CLi \cdot 2(C_2H_5)_2O$. Morton [9] described the formation of complicated complex compounds of organosodium derivatives. T.V. Talalaeva and K.A. Kocheshkov [10] indicated the formation of ternary complexes of phenyllithium with ether and lithium bromide. B.M. Mikhailov and N.G. Chernova [11, 12] prepared crystalline complexes of lithiumaryls with ether, amines, and dioxane and ascribed the following structure to them:



However, later on these authors [16] established that the latter complex contains one, not two, molecules of dioxane. As T.V. Talalaeva and K.A. Kocheshkov [13] have indicated, the structures of these compounds cannot be considered as strictly established, since the possibility of ternary complexes of the type $2ArLi \cdot LiBr \cdot 2(C_2H_5O)_2$ have not as yet been eliminated. The presence of lithium halide can always be assumed owing to the conditions of synthesis. The ability of lithiumalkyls to form unstable complex compounds with dioxane has been indicated in the work of N.G. Chernova and B.M. Mikhailov [16].

We prepared and characterized a complex of n-butyllithium and dimethyl sulfide. All operations during the preparation of butyllithium and the complex were carried out in an atmosphere of pure, dry nitrogen. The butyllithium was synthesized from butyl chloride and metallic lithium by the method described in [14]. Dimethyl sulfide was added dropwise (in excess) to a solution of butyllithium in petroleum ether (boiling up to 60°) at room temperature. With the addition of the sulfide, mild evolution of heat occurred, and an amorphous appearing precipitate separated and rapidly became crystalline. After 12-14 hours, the precipitate was filtered onto a glass filter in a stream of pure, dry nitrogen, washed with petroleum ether, dried, and transferred into ampoules for analysis or into a vessel for further investigation. Investigation of the structure of the complex was carried out by careful decomposition with water and quantitative determination of the products formed. Qualitative analysis established that the complex did not contain halide. Formation and decomposition of the complex can be represented by the equations:

$$n\text{-}C_4H_9Li + S(CH_3)_2 \rightarrow n\text{-}C_4H_9Li \cdot S(CH_3)_2$$
$$n\text{-}C_4H_9Li \cdot S(CH_3)_2 + H_2O \rightarrow n\text{-}C_4H_{10} + S(CH_3)_2 + LiOH.$$

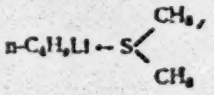
The gas liberated during the decomposition was collected in a Hempel pipet over a solution of mercuric chloride for absorption of the dimethyl sulfide. The remaining gas was transferred to a gas buret, and the butane content was determined by combustion over copper oxide in a quartz tube. The sulfide content was calculated after separation and weighing of the precipitate of $3HgCl_2 \cdot 2S(CH_3)_2$.

It was established that butane and dimethyl sulfide were liberated in nearly equimolar amounts during the decomposition of the complex.

Found (based on total products liberated) in %: lithium, 6.2; butane, 45.7; dimethyl sulfide, 48.1.

Calculated [according to $C_4H_9Li \cdot S(CH_3)_2$] in %: lithium, 5.5; butane, 45.3; dimethyl sulfide, 49.2.

The small deviation from equimolar ratios of the components could be due to possible errors in the analytical determinations, especially considering the extreme sensitivity of the complex to traces of moisture and oxygen. The results show that the crystalline compound isolated by us contained 1 mole of n-butyllithium and 1 mole of dimethyl sulfide, and the following structure is ascribed to it:



This complex gradually decomposes with the liberation of dimethyl sulfide at temperatures of 40-50° in a vacuum.

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Institute of High Molecular Compounds
Academy of Sciences, USSR

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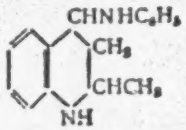
THE REACTION OF N-METHYLANILINE WITH ACETALDEHYDE

L.P. Zalukaev

(Presented by Academician I.N. Nazarov, May 5, 1956)

After we had established the structure of the product of the reaction of aniline with acetaldehyde (the so-called "Ekstein base") as 2-methyl-4-anilino-1,2,3,4-tetrahydroquinoline (I) [1,2] instead of 1,3-dianilino-2-butene (II), as originally proposed by Elbner [3], it became possible in principle to prepare similar quinoline derivatives from N-substituted anilines and acetaldehyde.



(I)

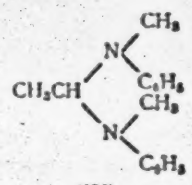
$C_6H_5NHCH(CH_3)CH=CHNHC_6H_5$ (II)

$CH_3CH(C_2H_5NC_6H_5)_2$ (IIa)

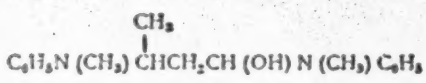
Up to the present, the reaction between N-alkylanilines and acetaldehyde in a neutral medium has not been studied. In the literature, there is only the almost century-old statement by Schiff [4] that N-ethylaniline and acetaldehyde form an oily product which did not yield to purification and to which, on the basis of an analysis of the chloroplatinate, he ascribed the formula (IIa). The products of the reaction of aniline and its derivatives with carbonyl compounds are presently of great interest and have found wide use as antioxidants and as accelerators in rubber vulcanization [5].

We have studied the reaction between methylaniline and acetaldehyde. As a result of this study, a condensation product with a m.p. of 83° has been obtained. It can be assumed that this product is one of four theoretically possible products (III-VI)

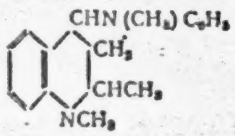
$C_6H_5N(CH_3)CH(OH)CH_3$ (III)



(IV)



(V)



(VI)

Since the substance melting at 83° did not possess an active hydrogen atom, which we attempted to detect by well-known methods, particularly by the action of methylmagnesium iodide in isoamyl ether, Formulas (III) and (V) can be dropped from further consideration. The reaction could proceed according to one of two routes:

$$2CH_3CHO + 2CH_3NHC_6H_5 = 2H_2O + C_{18}H_{22}N_2,$$

$$CH_3CHO + 2CH_3NHC_6H_5 = H_2O + C_{16}H_{20}N_2.$$

Determination of the molecular weight by two methods and an analysis of the product confirmed the formula $C_{18}H_{22}N_2$; i.e., the condensation product corresponds to Formula (VI). In addition, u.v. spectra of an 0.0001 molar alcoholic solution of 2-methyl-4-anilino-1,2,3,4-tetrahydroquinoline and of the newly prepared bimolecular product were very characteristic and similar (Figure 1). Thus, we have sound basis for accepting Formula (VI) and for assuming that the compound is 1,2-dimethyl-4-N-methylanilino-1,2,3,4-tetrahydroquinoline. For conclusive proof, it was necessary to convert it into the corresponding quinoline derivative. We had shown that 2-methyl-4-anilino-1,2,3,4-tetrahydroquinoline, melting at 126°, is easily decomposed by heating according to the equation

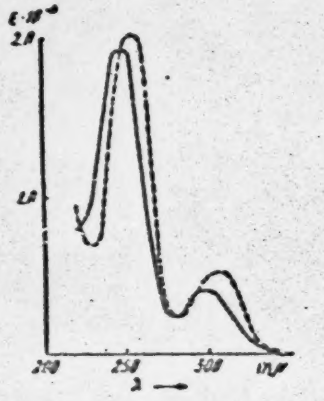
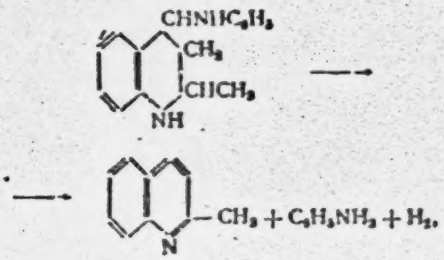
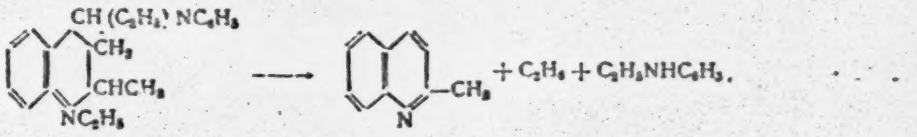


Fig. 1. Solid line, 2-methyl-4-anilino-1,2,3,4-tetrahydroquinoline; broken line, 1,2-dimethyl-4-N-methylanilino-1,2,3,4-tetrahydroquinoline.



on the basis of which was developed an acid-free method for the preparation of quinaldine [2]. On the other hand, N.S. Kozlov [6] developed a method for the preparation of quinaldine by a similar route starting with acetylene instead of acetaldehyde. N.F. Kryuk [7] extended Kozlov's reaction to ethylaniline and, although he did not describe the intermediate products, from the reaction he obtained, among other products, quinaldine and ethane, which confirms the course of the reaction according to



If Formula (VI), assumed for the substance melting at 83°, is correct, then from its decomposition we should have obtained quinaldine, methylaniline, and methane [8]. This was shown to be the case. We were successful in isolating both quinaldine and methylaniline from the liquid product. The gaseous products were not investigated. The oil, which Schiff observed to result from the reaction of acetaldehyde and ethylaniline and which was mentioned above, also gave an appreciable amount of quinaldine on distillation, which indicated its bimolecular nature.

EXPERIMENTAL

1. Preparation of 1,2-dimethyl-4-N-methylanilino-1,2,3,4-tetrahydroquinoline (VI). 11.6 ml of freshly distilled acetaldehyde was dissolved in 300 ml of alcohol, and to this solution were added successively 200 ml of water, 22 ml of freshly distilled N-methylaniline, and several crystals of the substance for seed.* Similar operations were carried out in parallel in another vessel. After standing two days, the crystals were combined

*The substance usually separates out in the form of a difficultly crystallizable oil. Without the use of seed crystals, crystallization sets in after two-three weeks at 10-12°. The first portion of crystals which were used in the future as seed, were obtained by this method.

and suction filtered. The weight of the crystalline material was 25 g. After recrystallization from 300 ml of alcohol, 15.8 g of white, well-formed crystals melting at 81° were obtained. A second recrystallization from alcohol did not change the melting point.

Found %: C 81.10; H 8.38; N 10.46. $C_{18}H_{22}N_2$. Calculated %: C 81.21; H 8.27; N 10.53. $C_{18}H_{26}N_2$. Calculated %: C 80.00; H 8.33; N 11.67.

Determination of molecular weight:

A. Ebullioscopic method

27.94 g chloroform 0.1011 g substance, $\Delta t = 0.053°$, M = 266.3
0.2074 g substance, $\Delta t = 0.111°$, M = 260.8
0.3102 g substance, $\Delta t = 0.158°$, M = 274.1

B. Cryoscopic method

23.60 g nitrobenzene 0.1901 g substance, $\Delta t = 0.220$, M = 262.0
0.2599 g substance, $\Delta t = 0.306$, M = 258.5

Found M = 267.4; 260.8. $C_{18}H_{22}N_2$. Calculated M = 266. $C_{18}H_{26}N_2$. Calculated M = 240.

2. Thermal decomposition of 1,2-dimethyl-4-N-methylanilino-1,2,3,4-tetrahydroquinoline. 11.6 g of the tetrahydroquinoline derivative was heated on a sand bath. The substance distilled over a wide range. The following fractions were collected: 1) to 197°, 0.5 g; 2) 197-245°, 8.0 g; 3) 245-256°, 0.5 g.

The oily residue remaining in the flask was not investigated further. The first fraction was practically pure monomethylaniline. Its acetyl derivative melted at 100-101°. A mixture with known N-methylacetanilide melted without depression of the melting point at 100-101°.

Found %: N 9.34. $C_9H_{11}ON$. Calculated %: N 9.40.

The third fraction was fairly pure quinaldine. Its picrate melted at 191-192°. A mixture with known quinaldine picrate melted without depression of the melting point at 192°. The methiodide melted at 199-200° (from alcohol).

Found %: N 5.05. $C_{10}H_9N \cdot CH_3I$. Calculated %: N 4.88.

The second fraction was redistilled. Two fractions were obtained: a) b.p. 210-230°, 4.2 g; b) b.p. 230-250°, 2.6 g.

Fraction a was mixed with 5 ml of acetic anhydride, refluxed for 30 minutes, and allowed to stand for a day in an open vessel. The crystals of N-methylacetanilide were suction filtered. Weight 1.2 g. After two recrystallizations from water using activated carbon, they melted at 99-100°. A mixture with a known preparation melted at 99-100°. The dark oil remaining after the separation of the crystals was dissolved in hydrochloric acid, alkalized, and steam distilled. The oil was extracted with ether, and the solvent was driven off. The weight of unpurified oil was 0.6 g. 0.5 g of quinaldine picrate was obtained by the action of a methanol solution of picric acid. M.p. 191-192° after recrystallization from alcohol. It melted without depression of the melting point when mixed with a known sample of the picrate.

Fraction b was dissolved in methanol. Picric acid in the same solvent was added to the solution. The weight of the picrate was 1.6 g. M.p. 191-192° after purification. A mixture with known quinaldine picrate melted at the same temperature.

3. Thermal decomposition of the product of the reaction of N-ethylaniline with acetaldehyde. 25 ml of ethylaniline was added to a solution of 11.6 ml of acetaldehyde in a mixture of 200 ml of water and 300 ml of alcohol. After standing two weeks, the dark oil was separated from the alcohol-water layer and distilled at ordinary pressure. B.p. 180-263°. Weight 6.7 g. The distillate – a transparent yellow liquid which rapidly darkened on storage – was dissolved in 50 ml of semi-concentrated hydrochloric acid, 50 ml of water was added to the solution, and the mixture was cooled with ice and diazotized with a solution of 3 g of sodium nitrite in 50 ml of water. After boiling, the cooled solution was treated with ether, and the water layer was alkalized, steam

distilled, and extracted with ether. After drying and elimination of the solvent, the oil was dissolved in methanol and converted to the picrate. M.p. 191-192°. A mixture with known quinaldine picrate and one with the picrate obtained in the preceding experiment both melted without depression of the melting point at 191-192°.

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Institute of Chemistry
Academy of Sciences, Latvian SSR

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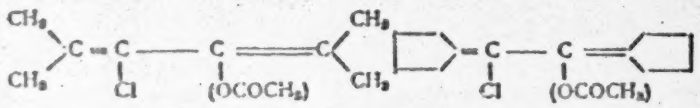
THE ALKYLATION OF BENZENE WITH HYDROXYISOPROPYLHYDROXY-CYCLOHEXYLACETYLENE DIACETATE IN THE PRESENCE OF $AlCl_3$

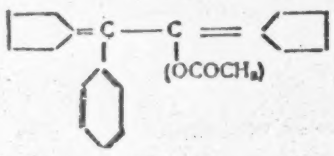
R.M. Lagidze and Sh.D. Kuprava

(Presented by Academician L.N. Nazarov, May 3, 1956)

It was shown in earlier investigations [1-3] that in the condensation of the acetates of 1,4-butynediol, tetramethylbutynediol, dihydroxycyclopentylacetylene, and dihydroxycyclohexylacetylene with benzene in the presence of anhydrous $AlCl_3$, the crystalline hydrocarbons $C_{14}H_{10}$, $C_{14}H_{16}$, $C_{18}H_{20}$, and $C_{22}H_{24}$, respectively, are formed. The intermediate chloroester 2,5-dimethyl-3-chloro-4-acetoxy-2,4-hexadiene (I) was isolated from the products of the condensation of tetramethylbutyndiol diacetate and benzene. The chloroester (I) was also observed in the reaction of anhydrous $AlCl_3$ with the diacetate directly. Under analogous conditions, the condensation of dihydroxycyclopentylacetylene diacetate with benzene gave, along with a hydrocarbon of the composition $C_{18}H_{20}$, the chloroester (II) and an aliphatic-aromatic ester (III), in which the double bonds may possibly be in the respective rings.



(I) (II)



(III)

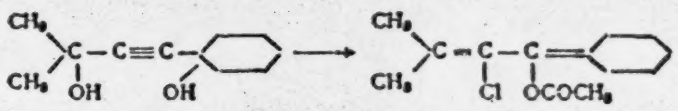
Isolation of these compounds presents the possibility of tracing the reaction by its stepwise course, of carrying out the last stage of the intramolecular cyclization of the ester (III) in neutral medium, and of obtaining the same hydrocarbon, $C_{18}H_{20}$. Thus, on the basis of the method of preparation and of a number of characteristic properties, the supposition was expressed that these hydrocarbons have as a common structural element a condensed system of a cyclobutene ring and a benzene ring. In all of the reactions enumerated above, symmetrical acetylenic glycols were used, the duplicate radicals of which are comparatively less favorable objects for proof of their common presence in the hydrocarbons synthesized by this method. In this regard, it seems to us that considerably more persuasive data would be obtained through the use of mixed acetylenic γ-glycols. For this purpose, hydroxylisopropylhydroxycyclohexylacetylene diacetate (IV) was used in the present work.

The initial glycol, m.p. 98°, was synthesized by a well-known method [4]. By acetylation of the glycol with the calculated amount of acetic anhydride, there was obtained a substance containing a triple bond, the results of the saponification of which agreed well with the theoretical for the diacetate of (IV): b.p. 98-100° (1 mm); d_4^{20} 1.0276; n_D^{20} 1.4650.

Found %: C 66.86; H 8.31. $C_{18}H_{22}O_4$. Calculated %: C 67.66; H 8.27.

The reaction was carried out under the same conditions as the condensation of diacetates of other γ-acetylenic glycols with benzene. From 25 g of the diacetate of (IV) was obtained 27 g of condensate, from which two fractions were isolated by distillation.

Fraction I, b.p. 87-90°/1.5-2 mm (25% yield with respect to total condensate), d_4^{20} 1.0308, n_D^{20} 1.4950, was 1-chloro-2-acetoxy-1-isopropylidene-2-cyclohexylidenethane (V). It was also obtained by the action of anhydrous $AlCl_3$ directly on the hydroxyisopropylhydroxycyclohexyl diacetate in a medium of dearomatized ligroin.



(IV) (V)

Found %: Cl 15.8; 15.64. $C_{13}H_{19}O_2Cl$. Calculated %: Cl 14.62.

The following were identified in the products of the oxidation of the chloroester (V) with potassium permanganate and also with chromium trioxide in glacial acetic acid: acetone, oxalic acid, and adipic acid.

Fraction II boiled at 130-138°/1.5-2 mm (about 30% yield); d_4^{20} 1.0242; n_D^{20} 1.5650; and it corresponded to $C_{17}H_{28}$ in elemental composition and molecular weight.

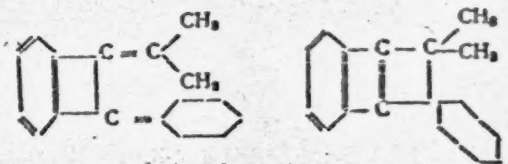
Found %: C 91.27; 91.06; H 9.24; 9.12. $C_{17}H_{28}$. Calculated %: C 91.07; H 8.93.

Molecular weights, found cryoscopically (in benzene), were 218 and 218.5. The molecular weight calculated for $C_{17}H_{28}$ is 224. MR_{found} 71.24, MR_{calc} 71.77.

The hydrocarbon $C_{17}H_{28}$, just as the other hydrocarbons enumerated above, did not decolorize bromine water or a weak alkaline solution of potassium permanganate. It was not hydrogenated over platinum catalyst under ordinary conditions at room temperature, and did not form a picrate. The carefully fractionated product crystallized very slowly on continued standing. The solid mass thus obtained, after a second recrystallization from ethyl alcohol, melted at 168-169°, and had properties similar to the original fraction.

Found %: C 91.33; 91.16; H 8.6; 8.7. $C_{17}H_{28}$. Calculated %: C 91.07; H 8.93.

Acetone and benzoic, adipic, and o-phthalic acids were isolated and identified (the latter only by means of the fluorescein reaction) from the products of the oxidation of the hydrocarbon $C_{17}H_{28}$ with chromium trioxide in glacial acetic acid. It should be noted that the formation of benzoic and phthalic acids in different ratios was also observed in the oxidation of the hydrocarbons $C_{14}H_{20}$, $C_{14}H_{16}$, $C_{18}H_{28}$, and $C_{20}H_{24}$. In the present case, on the basis of the oxidation results, it can be asserted that the hydrocarbon $C_{17}H_{28}$ contains a benzene nucleus and isopropyl and cyclohexyl radicals. It also follows from these data that these radicals are evidently connected through the respective carbon atoms to the benzene nucleus in the ortho positions. On the basis of all of the above, at the present time it would be difficult to assume for the hydrocarbon structural formulas other than those presented below (VI and VII).



(VI) (VII)

By dehydrogenation of the hydrocarbon fraction boiling at 130-133°/1-2 mm over Pd/C catalyst at 300°, a crystalline substance was obtained which gave a melting point depression of the order of 25-30° when mixed with anthracene. The study of this compound continues at the present time. Hydrogenation of the $C_{17}H_{28}$ hy-

drocarbon with Raney nickel at 100 atm. and 20-5° for 48 hours gave a colorless, oily liquid boiling at 129-131°/1 mm; d_4^{20} 0.9094; n_D^{20} 1.4904. Elemental analysis indicated the addition of 10 atoms of hydrogen to the $C_{17}H_{20}$ hydrocarbon.

Found %: C 87.04; 87.08; H 12.95; 12.90; MR 74.44. $C_{17}H_{30}$. Calculated %: C 87.18; H 12.82; MR 74.12.

Finally, it should be noted that oxidation of the $C_{17}H_{20}$ hydrocarbon with chromium trioxide in glacial acetic acid also gave, in the overwhelming majority of cases, a crystalline substance of neutral character melting at 203-204°. It was identical with the product of the oxidation of the $C_{14}H_{18}$ hydrocarbon, which was obtained by the condensation of tetramethylbutynediol diacetate with benzene. The melting point of a mixture of these substances was not depressed. For the material isolated, found, %: C, 77.66, 77.65; H, 6.44, 6.52.

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Institute of Chemistry
Academy of Sciences, GeorgSSR

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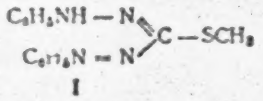
THE STRUCTURE OF THE METHYLATED FORMS OF DITHIZONE [DIPHENYLTHIOCARBAZONE] AND ITS DERIVATIVES

P.S. Pelkis and R.G. Dubenko

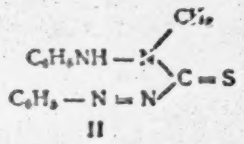
(Presented by Academician I.N. Nazarov, May 5, 1956)

In a previous paper by one of us [1], it was shown that methylation of dithizone by methyl iodide in alkaline medium leads to the monomethyl derivative. Two products having the same elemental composition were isolated by aluminum oxide chromatography. Preparation I was a yellowish orange color and had an absorption maximum at 430 mμ; Preparation II was a dark violet color, and had an absorption maximum at 545 mμ. It was established that Preparation II is converted into Preparation I at different rates in different solvents under the influence of light.

Starting from the concept of thione-thiol tautomerism of dithizone in solutions [1] and from data available in the literature on alkylation of compounds capable of undergoing keto-enol and amido-imidol tautomerism [2], it was proposed that methylation of dithizone leads to two methyl derivatives of dithizone:

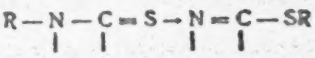


I



II

Considering that compounds with a thiono group are usually more deeply colored, Preparation II with an absorption maximum at 545 mμ was assumed to be the N-methyl derivative. In conformity with this, the isomerization of II in solvents was considered to be a transfer of the methyl group from the nitrogen to the sulfur [1]. Cases of isomerization in analogous triad systems



are described in the literature; however, they occur under severe conditions at temperatures of 200-300° and in the presence of catalysts [3-6].

Data from our further investigations showed that the experimental confirmation of the idea of methyl group migration was insufficient.

1. Compound II in benzene and other solvents was very sensitive to light. The period of half-life for the isomerization at 16° in direct sunlight was 150 minutes, and the activation energy was 5.4 kcal./mole. The period of half-life for the isomerization of Compound III (see Table 1) was 35 minutes, and the activation energy was 4.9 kcal./mole. It is known that the action of light has a substantial effect on cis-trans isomerization.

2. The characteristic Gattermann reaction on a thiono group – decolorization of colored thioketones by agitation with copper powder in xylene at room temperature [7] – gave a negative result during testing of the products of the methylation of dithizone. Under these conditions, dithizone is decolorized in 30-35 minutes.

3. Methylmercapto group reactions – heating with alcoholic alkali [8] – were positive for both isomers; i.e., methyl mercaptan, detected by its characteristic odor and by reaction with lead acetate, was liberated in both cases. The assumed N-methyl derivative (Preparation II) could not give a positive reaction for methyl mercaptan.

4. The yellow (I) and violet (II) methylation products of dithizone did not exchange their sulfur for radioactive sulfur (activity 4870 imp./mg/minute) when heated in xylene solution at 60 and 120° for 6 hours. Dithizone exchanges 74% of its sulfur under these conditions at 60°. The results of the experiments with radiosulfur apparently indicate that the sulfur in both isomers occurs as $\rangle C-S-C\langle$, i.e., both isomers contain a methylmercapto group. It is known that sulfur occurring as $\rangle C-SH$ or $\rangle C-S-C\langle$ does not exchange even under very severe conditions [9].

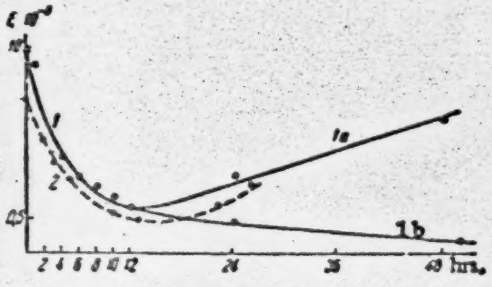


Fig. 1.

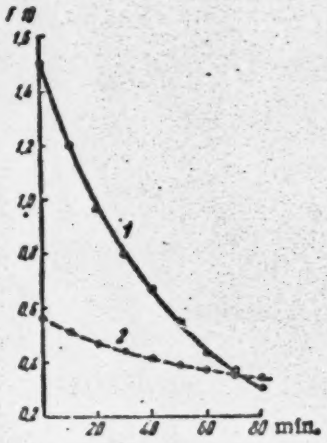


Fig. 2.

Fig. 1. 1) Preparation III; 1a) rate of isomerization in the dark, 1b) rate of isomerization in diffuse light. 2) Preparation II; rate of isomerization in diffuse light and in the dark.

Fig. 2. Rate of isomerization in sunlight at 16°; 1) Preparation III; 2) Preparation II.

5. Investigation of the infrared absorption spectra of I and II showed that the characteristic absorption band for the thione bond in the 1500-1550 cm^{-1} region was absent, while the absorption curve for dithizone had a band at 1508 cm^{-1}, which is characteristic of the thione bond [10, 11]. Thus, apparently the sulfur of both isomers occurs in methylmercapto groups. The measurements were carried out with a VIKS-3 vacuum spectrometer.*

Above all, the assumption that both isomers are methylmercapto derivatives in two stereoisomeric cis- and trans-forms conforms to the observed facts. Recently, Kuhn and Weitz studied the photochemical transformation of triphenylformazan $\begin{matrix} C_6H_5N=N \\ \diagdown \\ C_6H_5NH-N \end{matrix}\!\!>\!CC_6H_5$ in toluene under the influence of light. They established that the activation energy of the conversion of the yellow form to the red form is 4.6 kcal./mole, and the period of half-life of the isomerization is 5833 minutes. The authors explain this effect as cis-trans isomerization at the $-N=N-$ bond [12]. From the data cited, it is evident that the violet and yellow products of the methylation of dithizone are many times more sensitive to light than the corresponding isomers of triphenylformazan.

The dependence of the ratio of cis- and trans-isomers of the products of methylation and benzylation of dithizone in the same solvent on the nature and position of substituents in the phenyl groups was of interest. In Table 1 are presented derivatives of substituted dithizones which were prepared by us and which are not described in the literature. The syntheses were carried out under conditions described for Preparations I and II [1].

In Figure 1 are presented rate curves for the isomerization of Preparations II and III in benzene in dis-

*The measurements were carried out by A.F. Malnevy, to whom the authors express their appreciation.

perse daylight and in the dark. In Figure 2 are presented rate curves for the isomerization of II and III in benzene with illumination by sunlight (80,000 lux illumination) at 16°. The concentration of the preparations in the solutions was $6.6 \cdot 10^{-5}$ mol./liter. The isomerization rate was determined by measuring the optical density at maximum absorption of the preparation.

TABLE 1

No.	Empirical formula	M.p., °C, and appearance	Absorption maximum, mμ	Analysis, % N found	N calc.	S found	S calc.
III	$C_{14}H_{14}N_4S$	138 Yellow needles	436	18.67 18.6	18.79	10.43 10.36	10.76
IV	$C_{14}H_{14}N_4S$	129 Dark violet plates	545	18.62 18.66	18.79	10.36 10.44	10.76
V	$C_{16}H_{18}O_2N_4S$	109 Yellow needles	430	12.22 12.2	12.34	6.76 6.78	7.06
VI	$C_{21}H_{16}N_4S$	125–126 Dark violet color	545	15.94 16.00	16.18	8.86 8.95	9.26
VII	$C_{16}H_{18}O_2N_4S$	70–80 Yellowish orange crystals	436	10.31 10.42	10.36	5.97 6.1	6.04

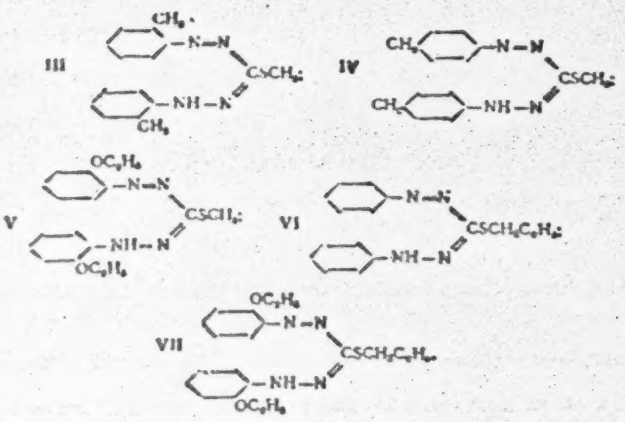
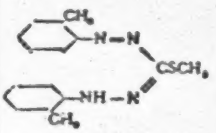
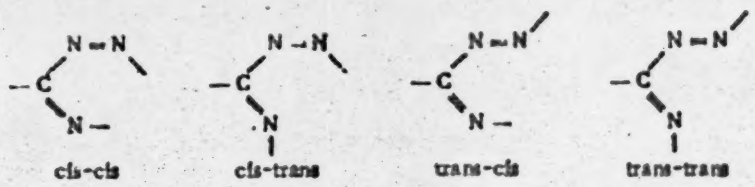


TABLE 2

Prep. No.	Formula	Isomer	Dipole moment	Prep. No.	Formula	Isomer	Dipole moment
I	C_6H_5-N / $CSCH_3$ / C_6H_5NH-N	Yellowish orange color	4.81	III		Yellow color	3.03
II	C_6H_5N-N / $CSCH_3$ / C_6H_5NH-N	Dark violet color	2.24				

In order to establish the cis-trans configurations of the violet and yellow products of methylation and benzylation of dithizone and substituted dithizones, the dipole moments of three preparations were measured in benzene at 20° (Table 2). We used theoretically calculated molecular refractions for calculating the dipole moments.

Four cis-trans isomers are theoretically possible, namely:



Considering the data from the measurements of the dipole moments and the fact of the experimental isolation of only two isomeric forms, it can be assumed that the yellow products of methylation of dithizone and its derivatives are cis-cis isomers, and the violet compounds are trans-trans isomers.

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Institute of Organic Chemistry
Academy of Sciences UkrSSR

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CYCLIC ISOMERS OF ACYLHYDRAZONES OF α,β-UNSATURATED KETONES AND THEIR TUBERCULOSTATIC PROPERTIES

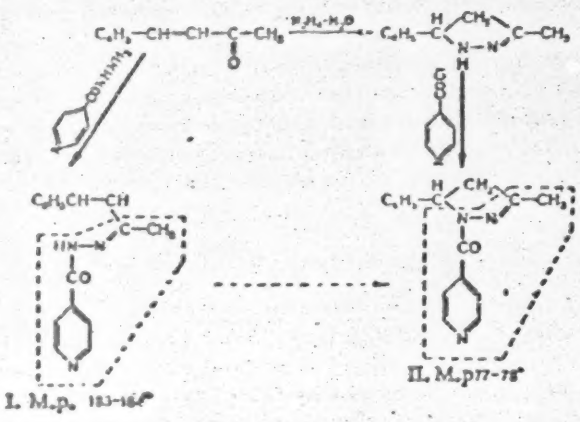
I.Ya. Postovsky and N.N. Vereshchagina

(Presented by Academician I.N. Nazarov, May 5, 1956)

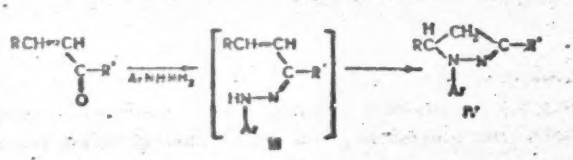
Isonicotinylhydrazide as well as a series of isonicotinylhydrazones are known to be highly active anti-tubercular compounds [1,2].

We synthesized several isonicotinylhydrazones of α,β-unsaturated ketones, among them the isonicotinylhydrazone of benzalacetone (I). The majority of these hydrazones possessed high tuberculostatic activity, even in concentrations of $1 \cdot 10^{-7}$.

In connection with the study of the relationship between structure and tuberculostatic activity, it was of interest to prepare the cyclic isomer of compound (I), 1-isonicotinyl-3-methyl-5-phenylpyrazoline, and to verify its anti-tubercular activity. We expected to prepare this compound by isomerization of the acyclic compound (I).



It is known that arylhydrazones of α,β-unsaturated ketones are easily isomerized to the pyrazoline compound, (IV), by heating in a solution of glacial acetic acid [3]. Sometimes the formation of the pyrazoline ring occurs so easily that the mere interaction of the α,β-unsaturated ketone with the arylhydrazone leads immediately to the formation of the cyclic compound.

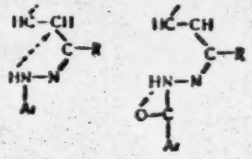


We attempted to cyclize the isonicotinylhydrazone of benzalacetone by refluxing in glacial acetic acid (under these conditions, the phenylhydrazone of benzalacetone easily gives 1,5-diphenyl-3-methylpyrazoline).

However, the cyclic isomer (II) was not obtained by this method, and the acylhydrazone was, in the main, recovered unchanged.

Similar isomerization experiments were carried out with the benzoylhydrazones of benzylideneacetone and furfurylideneacetone. The cyclic isomer, 1-benzoyl-3-methyl-5-phenylpyrazoline, previously described in the literature [4], was not formed by refluxing the benzoylhydrazone of benzylideneacetone in acetic acid. Neither was the benzoylhydrazone of furfurylideneacetone isomerized to the pyrazoline by refluxing with glacial acetic acid. Its cyclic isomer, 1-benzoyl-3-methyl-5-furylpyrazoline, prepared for purposes of comparison by benzoylation of 3-methyl-5-furylpyrazoline, differed in properties from the hydrazone. M.p. of the hydrazone, 146-147°; the known cyclic isomer melted at 73-74°.

Evidently, the acylhydrazones, in contrast to the arylhydrazones, are not able to undergo ring closure to the pyrazolines on refluxing in glacial acetic acid. Possibly, the hydrogen atom attached to the nitrogen of the acylhydrazone is "abstracted" in the direction of the carbonyl and has no tendency to add to the ethylene bond, while in the arylhydrazones it is easily shifted to the double bond.



Since the cyclic isomer which was of interest to us, 1-isonicotinyl-3-methyl-5-phenylpyrazoline, could not be prepared by cyclization of the hydrazone, we prepared it by the reaction of 3-methyl-5-phenylpyrazoline with hydrochloride of isonicotinyl chloride in ether-pyridine solution (see scheme). The pyrazoline obtained differed considerably in melting point and other properties from its acyclic isomer.

On testing of its tuberculostatic action, the 1-isonicotinyl-3-methyl-5-phenylpyrazoline (II) showed no appreciable activity in spite of the presence in the molecule of the same grouping as in the active acyclic isomer (this grouping is enclosed by the dotted lines of Formulas I and II).* This recalls the observation, made previously by us, of the loss of tuberculostatic properties of certain compounds on their conversion to cyclic products [5-7]. It is probable that the inactivity of the cyclic compound – the pyrazoline – is connected with the lack of the ability of the compound to hydrolyze at the azomethine bond and to give the active, original compound (the hydrazide), and it is possible that, for the emergence of activity, the presence of an unsubstituted amide group ($-C(=O)-NH-$), which is present in the acyclic isomer (I) and absent in the pyrazoline (II), is essential.

EXPERIMENTAL

Preparation of 1-benzoyl-3-methyl-5-furylpyrazoline. A solution of 1.5 g of furfurylideneacetone in 3 ml of alcohol was added gradually to 1 ml of hydrazine hydrate. The alcohol and the excess hydrazine hydrate were distilled under vacuum. To the 3-methyl-5-furylpyrazoline which remained, without first purifying it, 10 ml of NaOH and 1 g of benzoyl chloride were added with cooling. An alkaline medium was maintained during the reaction. After some time, the oil which separated crystallized. The yellow crystals were filtered and washed with water. After two crystallizations from aqueous alcohol, light yellow crystals (prisms) melting at 73-74° were obtained. Yield, 0.9 g (35%). The compound was easily soluble in alcohol, ether, acetone, chloroform, and benzene.

Found %: N 11.00, $C_{15}H_{14}O_2N_2$. Calculated %: N 11.02.

Preparation of 1-isonicotinyl-3-methyl-5-phenylpyrazoline. 5 g of the hydrochloride of isonicotinyl chloride (prepared from isonicotinic acid and thionyl chloride) was suspended in 15 ml of dry ether, and 10 ml of dry pyridine was added with cooling to the mixture. A solution of 4.5 g of 3-methyl-5-phenylpyrazoline [9] in 10 ml of dry ether was gradually added with cooling to the mixture. After 30-40 minutes, the precipitate

*For carrying out the bacteriological investigation of the compounds synthesized, we express our appreciation to Cand. Med. Science E.I. Cherikova (Sverdlovsk Tubercular Research Institute).

was filtered and washed with ether. On the addition of ether to the pyridine filtrate, a light yellow precipitate formed; this was filtered and washed with ether. Colorless plates melting at 77-78° were obtained after crystallization from aqueous alcohol with the addition of activated carbon. Yield, 1.7 g (23%). The material was easily soluble in alcohol, acetone, benzene, and chloroform, and was difficultly soluble in ether.

Found %: N 15.97. $C_{16}H_{15}ON_3$. Calculated %: N 15.84.

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S.M. Kirov Ural Polytechnical Institute

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ON THE ADDITION OF PHENOL TO BUTADIENE

Academician B.A. Arbuzov and L.A. Shapshinskaya

The reaction of phenols with dienes usually leads to the formation of cyclic products of the type of chroman and coumaran [1,2]. In certain cases, allylphenol-type compounds are obtained [3].

In 1951, Proell [4] investigated the alkenylation of aromatic compounds with butadiene in the presence of alkanesulfonic acids. Proell found that the reaction of phenol with butadiene in the presence of ethanesulfonic acid (10-12%) gives, in 50% yield based on butadiene, a mixture of substances of non-phenolic character (probably chromans) along with ortho- (?) and para- (?) butenylphenols. The structures of the products obtained were not established. The addition of phenol to butadiene can occur as both 1,2- and 1,4-addition.

In order to clarify the structures of these products, we repeated Proell's investigation. In the presence of methanesulfonic acid, phenol and butadiene gave only undistillable products. Ethanesulfonic acid in the amount indicated by Proell (10% of the weight of the phenol) led to the formation of undistillable products. The best yields of monobutenylphenols were obtained by the use of 2% ethanesulfonic acid as the catalyst (40% of the butadiene used).

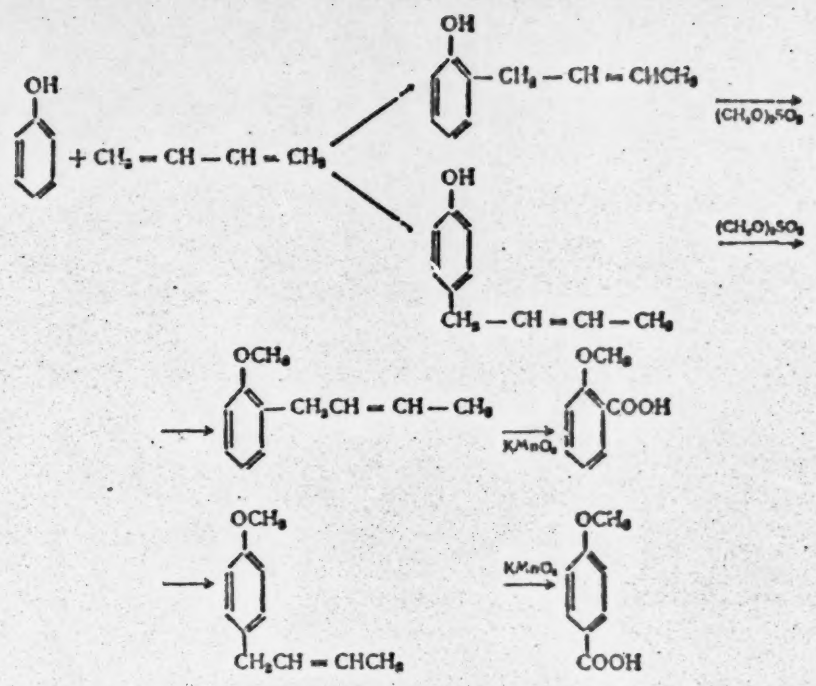
The non-phenolic part, which was separated by treatment of the low boiling fraction with alkali, gave the following fractions after repeated distillations: I) b.p. 86-88°/9.5 mm; n_D^{20} 1.5226; d_{20}^{20} 1.0228; MR_{Dfound} 44.17; $C_{10}H_{12}OF_3$ MR_{Dcalc} 44.22; II) b.p. 92-93°/9.5 mm; n_D^{20} 1.5315; d_{20}^{20} 1.0217; MR_{Dfound} 44.85. The fractions probably consisted of 2-ethylcoumaran and 2-methylchroman. Their structures were not proved. Evidently, these fractions are formed from o-butenylphenol, since specially conducted experiments on the cyclization of o-butenylphenol in the presence of hydrogen bromide and acetic acid gave similar products.

Distillation of the high boiling fraction of the products of the reaction of phenol with butadiene gave butenylphenols with the following constants: I) b.p. 90-92°/3 mm; n_D^{20} 1.5393; d_{20}^{20} 1.0047; MR_{Dfound} 46.06; $C_{10}H_{12}OF_4$ MR_{Dcalc} 45.84. II) b.p. 102-103°/3 mm; n_D^{20} 1.5390; d_{20}^{20} 1.0021; MR_{Dfound} 46.26. The first fraction was o-(2-butenyl)phenol, as was shown by oxidation of the methylated product with 0.5% potassium permanganate and with 5% potassium permanganate.

Acetaldehyde was isolated in the first case, and o-methoxybenzoic acid was isolated in the second.

The second fraction was p-(2-butenyl)phenol, since oxidation of its methylated product with 0.5% potassium permanganate gave acetaldehyde, and oxidation with 5% potassium permanganate gave anisic acid.

The reaction of phenol with butadiene in the presence of ethane-sulfonic acid and the proof of structure of the products can be represented by the following scheme:



EXPERIMENTAL

Addition of phenol to butadiene [4]. In a 2-liter flask fitted with a stirrer were placed 896 g (9.5 moles) of freshly distilled phenol and 20 g of ethanesulfonic acid [5]. 222 g (4.1 moles) of butadiene were passed into the flask at a temperature of 32° (water cooling). After treatment with water and distillation of the phenol under vacuum, the residue (244 g) was distilled using a Widmer dephlegmator.

The following fractions were obtained:

I 74-76°/6 mm; 32 g, 5.3% of the butadiene fed.

II 90-92°/3 mm; 29.3 g, 5% of the butadiene fed. o-Butenylphenol.

Found %: C 81.05; H 8.28. $C_{10}H_{12}O$. Calculated %: C 81.03; H 8.16.

III 102-103°/3 mm; 124 g, 20.7% of the butadiene fed. p-Butenylphenol, found %: C 81.32; H 8.39.

From Fraction I, after washing with alkali, was obtained a fraction boiling at 86-88°/9.5 mm:

Found %: C 80.30; H 8.05. $C_{10}H_{12}O$. Calculated %: C 81.03; H 8.16.

and a fraction boiling at 92-93°/9.5 mm:

Found %: C 80.50; H 8.05.

Methylation of o-butenylphenol. 20 g of o-butenylphenol was gradually introduced into 68 ml of 10% sodium hydroxide and then methylated with 20 g of dimethyl sulfate. The reaction product was steam distilled and then distilled with a Widmer dephlegmator. 17.7 g of product was obtained; b.p. 89-89.5°/6 mm; n_D^{23} 1.5225; d_{20}^{20} 0.9729; $MR_{D\,found}$ 50.82; $C_{11}H_{14}O$ F_4 $MR_{D\,calc.}$ 50.57.

Found %: C 81.59; H 8.61. $C_{11}H_{14}O$. Calculated %: C 81.45; H 8.7.

Methylation of p-butenylphenol (35 g) under similar conditions gave 32 g of p-methoxybutenylbenzene:

b.p. 80-80.5°/1.5 mm; n_D^{20} 1.5195; d_4^{20} 0.9619; $MR_{D\,found}$ 51.16. Found %: C 81.69; H 8.84. Oxidation of o-methoxybutenylbenzene and of p-methoxybutenylbenzene with 0.5% $KMnO_4$ gave acetaldehyde in both cases. 2,4-dinitrophenylhydrazone, m.p. 165-166° (a mixed sample with known 2,4-dinitrophenylhydrazone of acetaldehyde showed no depression of the melting point). Oxidation of o-methoxybutenylbenzene with 5% $KMnO_4$ gave o-methoxybenzoic acid, m.p. 99-100° [6] (mixed sample). Oxidation of p-methoxybutenylbenzene with 5% $KMnO_4$ gave anisic acid, m.p. 182-183° [7].

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V.I. Ulyanov-Lenin Kazan State University

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CATALYTIC CHLORINATION OF PROPANE

B.A. Krentsel, Academician A.V. Topchiev and D.E. Ilyina

The catalytic chorination of propane has been studied comparatively little, and, in the few studies that have been made, the attention of the investigators has been directed mainly toward the possibility of lowering the temperature and the conditions which would be required for this [1]. The literature sheds almost no light on product composition and its dependence on different conditions of catalytic chlorination.

EXPERIMENTAL

The composition of the propane feed, as determined by low temperature fractional analysis, was 95.3 wt. % C_3H_8, 4.2 wt. % C_2H_6, and 0.5 wt. % C_4H_{10}. The chlorination was carried out with gaseous chlorine (from a cylinder of liquified chlorine) in a previously described flow apparatus [2]. Heterogeneous catalysts – silica gel promoted with cupric chloride and an iron catalyst – and also a homogeneous reaction initiator – nitric oxide – were investigated as catalysts for the reaction.

Heterogeneous catalysts

The commercial silica gel used for the preparation of the silica gel-based catalyst was treated with hot, concentrated nitric acid to remove the colored impurities. The nitric acid-treated silica gel was washed with distilled water until the washings were neutral, and then was dried at a temperature of about 100°. Cupric chloride (20%) was deposited on this silica gel by impregnation with an aqueous solution of the salt and subsequent evaporation with constant stirring. The catalyst was dried at 110° to constant weight, and was then ready for use. The iron catalyst consisted of a stainless steel wire spiral of 2-mm diameter and the same height.

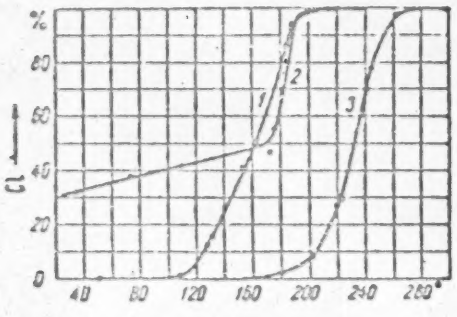

Fig. 1. Variation in chlorine consumption with temperature in the catalytic chlorination of propane. 1) $CuCl_2 \cdot SiO_2$ catalyst; 2) Fe catalyst; 3) empty tube.

Dependence of chlorine consumption on temperature in the reaction zone. The experiments on the dependence of the degree of chlorine consumption on reaction temperature were carried out with a two-fold excess of propane and at a space rate of reacting gases of about 60 hours^{-1}. The results of these experiments are presented in Figure 1.

The data show that the greatest activity was possessed by the iron catalyst, over which chlorination began at a low temperature and chlorine consumption reached more than 30% at 40°. These results are in complete agreement with our previously published experimental data on the chlorination of n-butane [3] with this same catalyst.

It is most probable that, in the case of the iron catalyst, a film of ferric chloride, which is formed on the surface of the catalyst, is responsible for the catalytic activity. This film can act as a chlorine transfer agent. As in the chlorination of n-butane, the mechanism can be elucidated as an evaporation of chlorine ions from the film into the gas space, and subsequent continuous renewal of the film.

In agreement with an hypothesis on the course of the heterogeneous reaction previously given in the literature, the catalytic action of cupric chloride deposited on silica gel (or other carrier) can be explained by the following exemplary mechanism:

a) $CuCl_2 \rightarrow CuCl + Cl$

b) $CuCl + Cl + C_3H_8 \rightarrow HCuCl_2 + C_3H_7$

c) $HCuCl_2 \rightarrow CuCl + HCl$

d) $CuCl + Cl_2 \rightarrow CuCl_2 + Cl$

e) $C_3H_7 + Cl \rightarrow C_3H_7Cl$

The effect of space rate and reactant ratio on the yield of propane chlorination reaction products. In order to clarify the effect of space rate on the yield of chlorination products, a special series of experiments was carried out at temperatures of 230-240° in which the space rate was varied within the limits of 60-200 hours^{-1}. Within these limits of space rate variation, the yield and composition of the chlorination products remained practically unchanged.

TABLE 1

The Effect of Reactant Ratio on Product Composition in Propane Chlorination

Experiment No.	Reaction temp., °C	Mole ratio $\frac{C_3H_8}{Cl_2}$	Space rate, hours^{-1}	Product composition, wt. % (from distillation data)		
				Monochlorides	Dichlorides	Trichlorides
			$CuCl_2 \cdot SiO_2$ catalyst			
142	237	2 : 1	126	44.3	42.1	13.6
144	240	1.5 : 1	101	49.1	38.1	12.8
146	242	4.05 : 1	200	32.5	47.7	19.8
147	245	3.97 : 1	203	32.5	48.3	19.2
148	242	1.2 : 1	88	42.4	41.8	15.8
149	237	3 : 1	160	46.8	40.0	13.3
			Iron catalyst			
159	230	2 : 1	120	73.6	21.1	5.3
160	235	4 : 1	200	80.7	14.7	4.6
161	235	1.09 : 1	83	55.2	33.5	11.3

The effect of propane-to-chlorine ratio is shown in Table 1.

Analysis of the data given in Table 1 provides a basis for considering that, under otherwise equivalent conditions, the yield of dichloro derivatives and trichloro derivatives was significantly higher over the copper-silica gel catalyst than during the work with the iron catalyst. With the latter catalyst, an increase in the excess of propane in the reaction mixture, as would be expected, caused a decrease in the yield of di- and trichlorides. On the other hand, this effect was expressed to a considerably lesser extent over the $CuCl_2 \cdot SiO_2$ catalyst.

Effect of temperature. In the work with the $CuCl_2 \cdot SiO_2$ catalyst, an increase in temperature to 300° caused severe decomposition of the reaction products with the formation of propylene and hydrogen chloride. At this temperature, the effluent gases contained 27.2% unsaturated hydrocarbons. Data showing the effect of temperature on product composition in propane chlorination over the iron catalyst are presented in Table 2.

The data obtained show a clear tendency toward a decrease in the yield of di- and trichlorides with an increase in reaction temperature. This correlates with our previous observations during the study of the chlorination of n-butane over heterogeneous catalysts.

Catalytic action of nitric oxide during chlorination of propane

The chain mechanism of the chlorination of paraffin hydrocarbons gives basis for the assumption that a substance which forms radicals easily must act catalytically on the chlorination reaction. This position is confirmed by data published in the literature on the chlorination of paraffinic hydrocarbons in the presence of tet-

raethyllead and azomethane [1, 4]. The catalytic action of nitrogen oxides in chain reactions in hydrocarbon oxidation, particularly in methane oxidation, is also known [3].

TABLE 2

The Effect of Reaction Temperature on Chlorination Product Composition. Iron Catalyst*

Experiment No.	Reaction temp., °C	Mole ratio $\frac{C_nH_{2n}}{Cl_2}$	Space rate, hours^{-1}	Product composition, wt. % (from distillation data)		
				Monochlorides	Dichlorides	Trichlorides
159	230	2:1	120	73.6	21.1	5.3
163	270	2:1	120	79.0	17.6	3.4
165	300	2:1	113	80.7	15.3	4.0
167	347	2:1	120	80.8	16.5	2.7
160	235	4:1	200	80.7	14.7	4.6
162	270	4.07:1	200	88.2	9.7	2.1
164	300	3.96:1	203	88.1	9.5	2.4
166	347	4:1	200	83.0	9.5	1.5

*In all of the experiments the effluent gases contained no unsaturated hydrocarbons.

In the opinion of V.V. Voevodsky and V.N. Kondratyev [6], the catalytic action of NO_2 in chain reactions of hydrocarbon oxidation is explained by the occurrence of the process

$$RH + NO_2 \rightarrow R + HNO_2.$$

According to approximate calculations, this reaction gives a certain energy gain in comparison with simple cleavage of the RH molecule into R and H. Because of this, R radicals are formed more easily in the presence of NO_2 than in its absence.

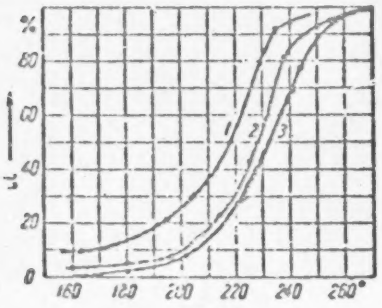

Fig. 2. Variation in chlorine consumption with temperature during the chlorination of propane in the presence of NO_2. 1) 2% NO_2; 2) 1% NO_2; 3) thermal reaction.

We were the first to demonstrate the catalytic effect of nitric oxide in the chlorination of n-butane. Later on, this phenomenon was confirmed by V.A. Nekrasova and N.I. Shulkin during a study of the chlorination of higher molecular weight paraffinic hydrocarbons.

In order to confirm the catalytic role of nitric oxide during propane chlorination, the reaction between chlorine and propane was carried out in the usual flow-type apparatus with the addition of nitric oxide to the reaction mixture in amounts of 1-2%. The experiments were carried out with a three-fold excess of hydrocarbon in the reaction mixture and at a space rate of 50 hours^{-1}.

The results obtained are presented in Figure 2. As can be seen from the graph, also in the case of propane chlorination there is observed a clearly expressed catalytic effect of the nitric oxide which leads to a higher percentage chlorine consumption than in the purely thermal process carried out under otherwise equivalent conditions.

As regards the mechanism of the catalytic effect of NO_2 in the chlorination of paraffinic hydrocarbons, the most probable is the formation of NOCl, which then liberates atomic chlorine: $NOCl \rightarrow NO + Cl$. The energy required to rupture the N–Cl bond is 36 kcal/mole, while the energy required for the Cl–Cl bond is 58 kcal/mole. Thus, when NO_2 is used as a homogeneous catalyst for the chlorination reaction, there is an energy gain of 22 kcal/mole. This mechanism is in agreement with the thesis expressed by N.N. Semenov in his recent work [8].

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CHEMICAL STUDY OF THE ALKALOIDS OF THE SECURINEGA SEMI-SHRUB SECURINEGA SUFFRUTICOSA (PALL.) REHD.

V.I. Muravyeva and A.I. Bankovsky

(Presented by Academician I.N. Nazarov, May 5, 1956)

The Ussuri expedition of the All-Union Institute of Medicinal and Aromatic Plants first established the presence of appreciable amounts of alkaloids in the leaves and young stalks of the securinega semi-shrub Securinega suffruticosa (Pall.) Rehd., family Euphorbiaceae[1]. The securinega semi-shrub is a bush 1.5-2 meters high which grows wild in the Ussuri region. The plant raw material (leaves and shoots) was collected in the flowering and fruit-bearing stages. Isolation of the total alkaloids was carried out by the dichloroethane method; the yield of alkaloids from the leaves was 0.38%, and the yield from the shoots was 0.19%, both on the basis of the air-dried raw material. From the total alkaloids was isolated an individual crystalline base melting at 139-140°, $[\alpha]_D^{20} = 1042.3°$, (ethanol, C = 1), of the composition $C_{13}H_{15}O_2N$. This base crystallized from ethanol in the form of pale yellow prisms which were readily soluble in chloroform, difficultly soluble in ethyl ether, petroleum ether, and acetone, and slightly soluble in cold water.

It forms easily crystallizable salts with mineral and organic acids: hydrochloride m.p. 230°, nitrate m.p. 205°, sulfate m.p. 128°, picrate m.p. 218°, picrolonate m.p. 194°, chloroaurate m.p. 168°, chloroplatinate m.p. 210°, and perchlorate m.p. 208°.

Determination of N-methyl, methoxy and hydroxy groups showed that they are not present in the molecule of the base. A negative reaction was obtained in a qualitative test for the dioxymethylene group; keto group derivatives (semicarbazone, phenylhydrazone, and oxime) also were not obtained. The base dissolved completely on heating in alkaline solution, and the original base was liberated on neutralization with acids, which makes it possible to assume the presence of a lactone group. Spectral analysis in the i.r. and u.v. regions showed the presence of a lactone group and of conjugated double bonds in an aromatic or heterocyclic nucleus and the absence of NH and OH groups in the molecule. The composition and properties of this base and the melting points of its salts provide a basis for assuming that it is a new, previously undescribed base which we have named securinine.

EXPERIMENTAL

Extraction of the total alkaloids. 2 kg of the powdered leaves of Securinega were moistened with 200 ml of 10% aqueous ammonia and exhaustively extracted with dichloroethane (1:7). The dichloroethane extract, which contained the alkaloids and other extractable substances, was treated several times with a 10% solution of sulfuric acid until extraction of the alkaloids was complete. The sulfuric acid solution of alkaloids was alkalized with 25% ammonia, and the alkaloids were extracted as the bases with chloroform. The chloroform solution was dried with anhydrous sodium sulfate. After distillation of the solvent, the alkaloids were obtained in the form of a brown crystalline mass; 7.6 g were obtained, which amounted to a yield of 0.38%. In all, 50 kg of raw material was treated by this method, and 190 g of total alkaloids was obtained.

Isolation and purification of securinine. 20 g of total alkaloids was placed in a round-bottomed flask fitted with a reflux condenser and was repeatedly treated with 200-ml portions of boiling ethyl ether for 30 minutes each time; after each treatment, the solvent was decanted, and a new portion of solvent was added to the residue. Six such decantations were made, and 1.2 liters of ethereal solution of alkaloids was obtained,

After distillation of the ethyl ether, a quantity amounting to 7.9 g of crystalline alkaloids was obtained, which amounted to 39.5% of the original amount or 0.15% claculated on the dry herb. The residue, which was insoluble in ether, was a dark brown color and did not undergo reactions of alkaloids.

The purified total alkaloids were treated with boiling ethanol. On cooling, yellow prismatic crystals of securinine were precipitated, which, after separation from the solvent, two-fold recrystallization from ethanol, and drying in a pistol at 100°, had a melting point of 139-140°.

The alcohol exhibited optical activity:
0.1600 g of material in 16 ml of ethanol, $\underline{l}$ = 1.89 dm.
α = 19.7°, $[\alpha]_D^{23}$ = 1042.3°

0.1000 g of material in 20 ml of chloroform, $\underline{l}$ = 1.89 dm.
α = 10.45°, $[\alpha]_D^{23}$ = 1105.8°.

Elemental analysis of securinine gave the following results:

Found %: C 71.71; 71.74; H 7.02; 7.03; N 6.46; 6.52. $C_{13}H_{15}O_2N$. Calculated %: C 71.87; H 6.95; N 6.45.

Determination of the molecular weight cryoscopically in benzene gave the following results:

Found %: M 203.00; 200.19. $C_{13}H_{15}O_2N$. Calculated %: M 217.16.

Thus, the alkaloid which was isolated from the leaves of the securinega semi-shrub and which was named securinine has the composition $C_{13}H_{15}O_2N$.

Preparation of derivatives

1. Hydrochloride. Anhydrous acetone saturated with hydrogen chloride to a weakly acidic reaction was added to 0.2 g of securinine dissolved in acetone. White crystals of the hydrochloride were precipitated by the addition of ethyl ether. After recrystallization from alcohol, the hydrochloride had a m.p. of 230°, $[\alpha]_D^{23}$ = 259.2° (ethanol, C = 0.5).

2. Nitrate. Ethyl ether containing concentrated nitric acid was added dropwise to a solution of securinine in ethyl ether. The resulting nitrate, after recrystallization from alcohol had a m.p. of 205°, $[\alpha]_D^{23}$ = 312.12° (ethanol, C = 0.5).

3. Sulfate. Ethyl ether containing concentrated sulfuric acid was added dropwise to a solution of securinine in ethyl ether. The precipitated sulfate, after recrystallization from alcohol, had a m.p. of 128°.

4. Picrate. An alcoholic solution of picric acid was added to an alcoholic solution of securinine. The orange prisms of picrate melted at 218° after recrystallization from alcohol.

5. Picrolonate. An alcoholic solution of picrolonic acid was added to an alcoholic solution of securinine. Upon brief standing, orange prisms of the picrolonate were formed, which, after recrystallization from alcohol, melted at 194°.

6. Chloroaurate. A solution of auric chloride in 1.0 N sulfuric acid was added dropwise to a solution of securinine in 1.0 N sulfuric acid. On brief standing, brownish-gold needles were precipitated; m.p. 165°.

7. Chloroplatinate. A solution of platinic chloride in 5% HCl was added dropwise to a solution of securinine in 5% HCl. The resulting precipitate was recrystallized. On standing, gold needles of securinine chloroplatinate precipitated; m.p. 210°.

8. Perchlorate. A saturated aqueous solution of sodium perchlorate was added dropwise to an alcoholic solution of securinine. After several minutes, white needles of securinine perchlorate precipitated, which, after recrystallization from alcohol, melted at 208°.

Determination of functional groups

Determination of N-methyl and methoxy groups (by the method of Viebŏck and Brecher) and also of hy-

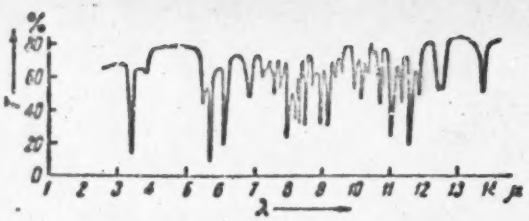

Fig. 1. Infrared spectrum of securinine (in glycerine).

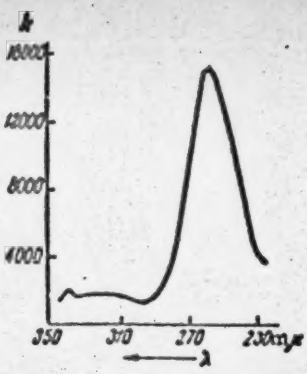

Fig. 2. Securinine absorption spectrum in the ultraviolet.

droxyl groups (by the method of Tserevitinova) showed that these groups are not present in the securinine molecule [2]. Negative results were obtained in a qualitative test for dioxymethylene groups (with phloroglucine in sulfuric acid), and derivatives of the keto group likewise were not obtained (semicarbazone, phenylhydrazone, oxime) [3].

For lactone group determination, the securinine was hydrolyzed [4]. 1 g of securinine was placed in a 50-ml round-bottomed flask fitted with a reflux condenser, 15 ml of a 10% solution of KOH in methanol was added, and the mixture was refluxed on a water bath for 3 hours. The methanol was then distilled to dryness, and the residue, which was an oily mass, was dissolved in 10 ml of water. The solution was neutralized and treated 3 times with ether. After distillation of the ether, a yellow crystalline substance was obtained, which, after two-fold recrystallization, melted at 139-140°. The nitrate of this substance melted at 205°. These characteristics are characteristic of securinine. This provides basis for the assumption that the oxygen in the securinine molecule is in a lactone group. The presence of a lactone group (δ-lactone) was also confirmed by spectral analysis of securinine in the infra red region. Moreover, spectral analysis in the i.r. and u.v. regions showed that there are conjugated double bonds in an aromatic or heterocyclic nucleus in securinine, and that NH and OH groups are absent (see Figures 1 and 2).*

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COMPOUNDS OF CONSTANT AND VARIABLE COMPOSITION IN THE SYSTEM SODIUM SUPEROXIDE – SODIUM OXIDE

T.V. Rode and G.A. Golder

(Presented by Academician I.I. Chernyaev, November 5, 1955)

Sodium superoxide (NaO_2) was first synthesized in 1936 by I.A. Kazarnovsky [1]. Kleinberg and coworkers published a series of works on the synthesis, analysis, and magnetic measurements of NaO_2 [2-4] and its reactions with nitrates in liquid ammonia [5,6]. A series of authors [1, 7, 8] ascribed to sodium peroxide a cubic structure of the type of sodium chloride; however, more recently [9] it has been found, by the method of single crystal x-ray diffraction, that at room temperature NaO_2 has the irregular structure of pyrite with the parameter, established by G.S. Zhdanov and Z.V. Zvonkova [8], a = 5.44 A.

In 1953, it was established by one of us [10] that NaO_2 has two low temperature polymorphic modifications with transitions at −80° and −43°. In the same year, works appeared which confirmed our data by other methods [9, 11, 12]. Carter and Templeton [9] established that between −80 and −43° NaO_2 has the pyrite structure with the parameter a = 5.46 A, and below −80° it has the marcasite structure with the parameters a = = 4.26 A, b = 5.54 A, and c = 3.44 A. Neiding and Kazarnovsky [13] found a maximum on the magnetic susceptibility-temperature curve at −80°. The heat capacity [14] and entropy [12] of NaO_2 have been measured.

EXPERIMENTAL

We carried out a physicochemical investigation of sodium peroxide and superoxide (chemical, thermal, and x-ray analyses; temperature-composition curves, obtained by continuous determination of the loss in weight by means of a thermobalance, and decomposition polytherms), and a temperature-composition diagram of the system NaO_2–Na_2O was constructed. The methods used have been described in previous papers [15, 16]. During the course of the work, the samples were carefully isolated from the effects of atmospheric moisture and CO_2.

We investigated two preparations of sodium peroxide having the following compositions:

No.	NaO_2, %	Na_2O_2, %	Total NaOH and Na_2CO_3, %
1	76.50	21.95	1.55
2	85.62	12.88	1.50

Since sodium peroxide is a decomposition product of the superoxide, its presence had no effect on the form of the thermograms. Lines of both NaO_2 and Na_2O_2 were observed on the radiograms of both of the original preparations. Compositions given later of the intermediate decomposition products (to the composition Na_2O_2) were recalculated on the basis of pure Na_2O_2.

In Figure 1 are presented the thermogram (1), recorded in a Stepanov cell, and the decomposition polytherm (2) for Preparation No. 1, and similar curves for Preparation No. 2 are presented in Figure 2.

Time is plotted on the abscissa of both curves; the ordinate for the thermograms is the temperature difference between the sample and the standard (MgO), while the ordinate for the decomposition polytherms is the number of ml of oxygen (s.t.p.) liberated from the sample at a given intermediate time.

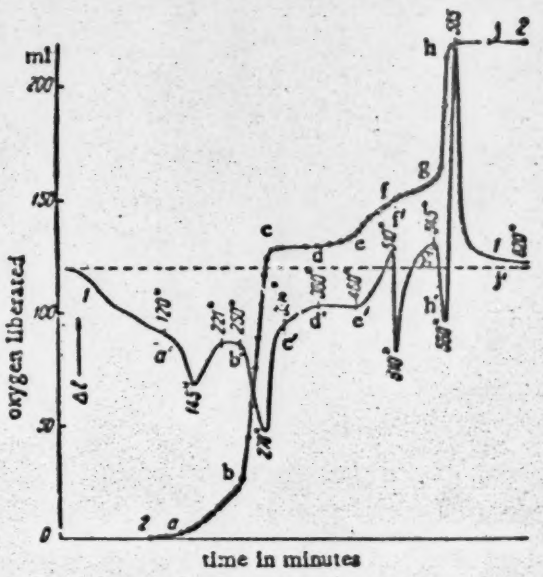

Fig. 1. Thermogram (1) and decomposition polytherm (2) of sodium superoxide (Preparation 1).

The following effects are observed on the thermogram (1) of Figure 1: at about 120° there begins an endothermic effect corresponding to the decomposition of NaO_2 with the formation of a continuous series of solid solutions up to the limiting composition, which corresponds to the molecular formula $Na_2O_{2.68}$. The formation of the solid solutions is confirmed by the continuous source of the decomposition polytherm to the indicated composition over the portion of the curve a–b (Curve 2) in the region of this effect. x-Ray examination of the preparation before and after heating in the Stepanov cell for 26 hours at 138°, i.e., in the region of these solid solutions, disclosed a small displacement in the interference lines (see Table 1) which confirmed the results of our polythermal analysis. As may be seen from the table, there is a decrease in the cell parameters, which corresponds to solid solution "deficiencies", which is precisely what happens in the present case.

TABLE 1

x-Ray Measurements on Preparation No. 2 in Its Original State and After Heating at 138°

Interplanar distance, A		Difference	
Original preparation	After heating	In A	In %
3.0739	3.0636	0.0103	0.33
2.7670	2.7559	0.0111	0.40
2.5689	2.5571	0.0118	0.46
1.9564	1.9406	0.0158	0.81
1.8211	1.8054	0.0157	0.86
1.6613	1.6475	0.0138	0.83
1.5976	1.5834	0.0142	0.89
1.2701	1.2586	0.0115	0.91
1.0607	1.0470	0.0137	1.29

Beginning at 250° on the thermogram (Figure 1) is a highly endothermic effect corresponding to the decomposition of the limiting solid solution composition to sodium peroxide, Na_2O_2. On the decomposition polytherm there is observed an almost vertical portion, b–c, which indicates vigorous evolution of oxygen in the

region of this effect. Chemical analyses of preparations heated to 320°, i.e., to a temperature immediately after this effect, confirmed that the decomposition product was Na_2O_2. NaO_2 lines disappeared from the powder radiograms, and only the lines of Na_2O_2 remained.

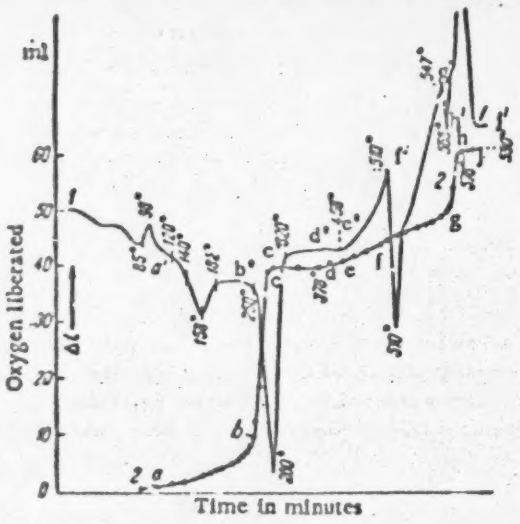

Fig. 2. Thermogram (1) and decomposition polytherm (2) of sodium superoxide (Preparation 2).

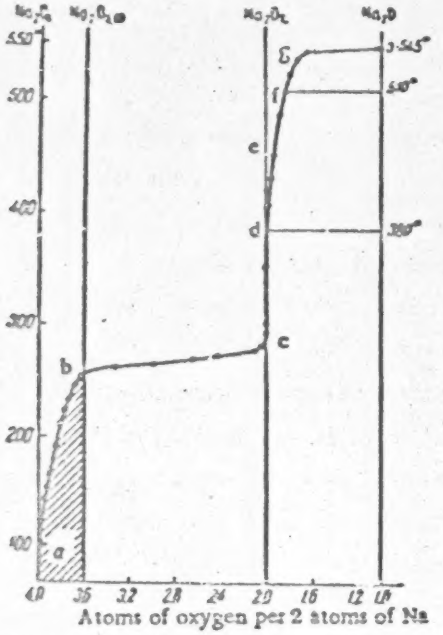

Fig. 3. Temperature – composition diagram (heating rate 5.5-6°/minute) for the system NaO_2–Na_2O.

Above 380°, a slow liberation of oxygen from the Na_2O_2 begins (d–e, Curve 2). This liberation is not accompanied by an appreciable thermal effect. At about 460° (point e, Curve 2), an increase in the rate of oxygen liberation is observed, and, beginning at this temperature, the sodium oxide, formed by the decomposition of the peroxide, reacts with the glass of the pyrex cell, as has been established by us. A small exothermic effect on the thermogram at 460-510° (e–f) corresponds to the latter process. The large endothermal effect of the melting of Na_2O_2 is observed on the thermogram at 510°. Between 510 and 545°, further decomposition of the peroxide continues, taking place in the molten state (f–g, Curve 2). At 545-560°, an endothermic effect is observed on the thermogram, and the decomposition polytherm shows a second intense liberation of gas (g–h), indicating that this effect corresponds to the decomposition of the melt with the liberation of all of the active oxygen and the formation of solid sodium oxide.

The latter effect proceeds directly into a large exothermic effect at 560-585°, which corresponds, as we have established, to the reaction of the sodium oxide formed with the glass of the cell. A similar effect was observed by us during an investigation of lithium peroxide [15, 16]. The presence of a similar effect when the thermogram was recorded using a stainless steel cell showed that the Na_2O, in contrast to Li_2O [15, 16], reacts not only with the glass, but also with stainless steel, and only the use of metallic nickel cells would make it possible to avoid this reaction and the exothermic effect on the thermograms.

On the thermogram of Preparation No. 2 (see Figure 2) there was an additional exothermic effect at 85-95° corresponding to enlargement of the superoxide crystals, as was shown by a radiogram of superoxide Preparation No. 2 heated for 2 hours at 100°. There were breaks in the continuity of the interference lines of the radiogram. This indicates that the exothermic effect at 85-95° corresponds to enlargement of the NaO_2 crystals.

The remainder of the thermograms and decomposition polytherms of Preparations Nos. 1 and 2 were almost identical. There was one difference in that the exothermic effect of the decomposition of the residual melt, beginning here at 547°, is wedged into the large exothermic effect of the reaction.

The polythermal curves of the loss in weight with temperature confirmed the results obtained by differential thermal analysis and x-ray analysis.

In order to determine the temperature-composition diagram for the system NaO_2-Na_2O, samples of the preparations of NaO_2 were heated in Stepanov cells to various temperatures in the range 150 to 565° with parallel recording of the thermograms and the decomposition polytherms; after this, analyses for active oxygen were made on the products obtained, and radiograms were taken of certain of them.

The temperature – composition diagram for the system NaO_2-Na_2O is presented in Figure 3. It is not an equilibrium diagram, and corresponds to a rate of heating of 5.5-6°/minute.

The cross-hatched portion, a–h, of the diagram between 100 and 250° corresponds to a continuous series of solid solutions with the limiting composition corresponding to the molecular formula $Na_2O_{2.62}$. Beginning at 250°, there is an intensive decomposition of the solid solution to Na_2O_2. With an increase in temperature, the latter begins to decompose slightly while still in the solid state (d–e–f). At 510°, the undecomposed sodium peroxide melts, and its slow decomposition continues in the liquid state to 545° (f–g). At the latter temperature, there was a vigorous decomposition of the remaining liquid peroxide with the formation of solid sodium oxide. A heterogeneous region of molten sodium peroxide and solid sodium oxide is observed on the diagram between 510 and 545°.

To sum up, the study of the system NaO_2-Na_2O established the existence of the following phases of constant composition: three modifications of NaO_2 with transition temperatures of −80 and −43°, Na_2O_2, and Na_2O, and also a single phase of variable composition in the range from Na_2O_4 to $Na_2O_{2.62}$ having the lattice of sodium superoxide. The formation of a compound of the composition Na_2O_3 under our conditions was not established.

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N.S. Kurnakov Institute of General and Inorganic Chemistry – Academy of Sciences, USSR

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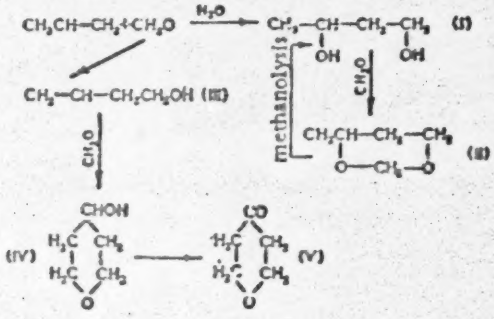
*T.p. = C.B. Translation pagination.

DUAL REACTIVITY IN REACTIONS OF OLEFINS WITH ALDEHYDES

M.I. Faberov

(Presented by Academician L.N. Nazarov, May 5, 1956)

Olefins react easily with formaldehyde, and some also with acetaldehyde and other aldehydes, in an aqueous medium in the presence of an acid [1]. During a study of this reaction using a number of reactants, we have shown that two series of products are formed. The basic products of these reactions are diols and, chiefly, products of the further reaction of the diols with the aldehydes: cyclic acetals – alkyl-1,3-dioxanes. Thus, in the reaction of propylene with formaldehyde (Scheme 1) the basic reaction product is 4-methyl-1,3-dioxane (II).

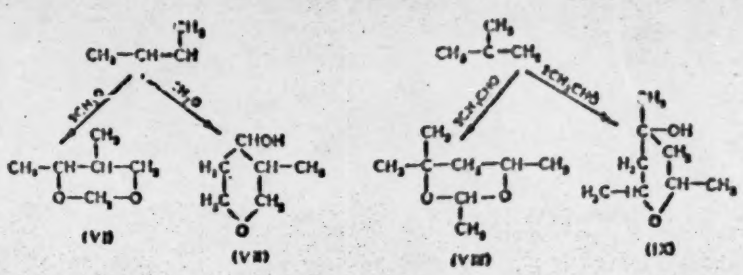


Scheme 1

which is formed along with a certain amount of 1,3-butanediol (I). The other series of reaction products comprise unsaturated alcohols and, chiefly, the products of their further reaction with the aldehyde: cyclic alcohols, derivatives of hydroxytetrahydropyran. In the reaction of propylene with formaldehyde, in addition to the first series of products, allylcarbinol is formed in small amounts and 4-hydroxytetrahydropyran (IV) is formed in quite appreciable amounts. Structure (IV) was proved by oxidation to tetrahydro-γ-pyrone and by a series of other reactions [2].

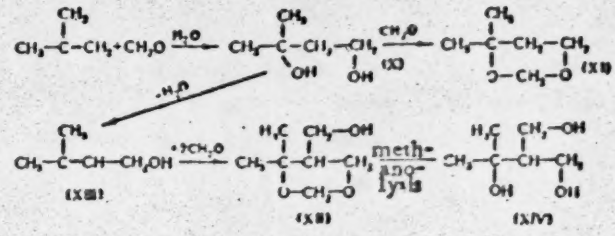
Other olefins react similarly. Thus the basic product of the reaction of 2-butene with formaldehyde is 4,5-dimethyl-2,3-dioxane (VI), which is formed along with a certain amount of 3-methyl-4-hydroxytetrahydropyran (VII). In the reaction of isobutylene with acetaldehyde, along with the basic product 2,4,4,6-tetramethyl-1,3-dioxane (VIII), a certain amount of 2,4,6-trimethyl-4-hydroxytetrahydropyran (IX) is formed.

In the reaction of isobutylene with formaldehyde, only one series of products is formed, diol derivatives – 3-methyl-1,3-butanediol (X). The basic product of the reaction, along with a certain amount of (X), is 4,4-dimethyl-1,3-dioxane (XI). In addition, a certain amount of a cyclic alcohol containing a dioxane ring, 4,4-dimethyl-5-hydroxymethyl-1,3-dioxane (XII), is found in the reaction products.



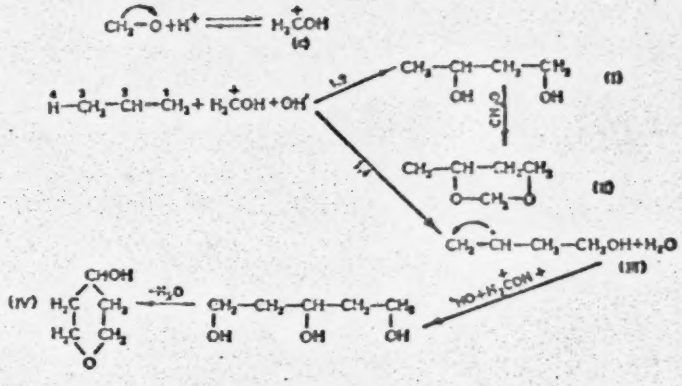
Scheme 2

Proof of structure of (XII) was by, among other reactions, methanolysis to the triol (2-hydroxymethyl-3-methyl-1,3-butanediol (XIV)) (Scheme 3).



Scheme 3

The mechanism of the formation of two series of products during the reaction of olefins with formaldehyde can be explained by starting from the hypothesis, proposed by A.N. Nesmeyanov and M.I. Kabachnik [3], concerning the causes of dual reactivity. The olefins considered are characterized by the presence of $\sigma\pi$-conjugation, which imparts the ability to react at the 1,2- and 1,4-bonds. By way of example, let us consider the mechanism of these reactions for the case of the reaction of propylene with formaldehyde (Scheme 4).



Scheme 4

According to the presently widely accepted concept of the mechanism of acid catalysis, the role played by the acid leads to the formation of an intermediate carbonium ion. In the present case, the acid gives up a proton to form a carbonium ion from the formaldehyde (a). The reaction proceeds mainly at the 1,2-bond: the formaldehyde carbonium ion (a) adds to carbon atom 1; there arises at the second carbon atom a positive carbonium reaction center which, reacting with water, adds an hydroxyl group (with the liberation of a proton). As a result of the 1,2-addition, 1,3-butanediol is formed [1]. In the second case, the addition of the carbonium ion (a) to carbon atom 1 is accompanied by a shift of the reaction center to the fourth atom; hydrogen atom 4

Compound No.	Name	Yield, % of theoretical	Constants				MR_D		Analysis, %		Literature
			B.p., °C	Pressure, mm Hg	d_4^{25}	n_D^{20}	found	calc.	found	calc.	
	Propylene with formaldehyde										
(I)	1,3-Butanediol	3—5	203—204	760	1.0197	1.4433	23.41	23.72		$C_4H_{10}O_2$	[5]
(II)	4-Methyl-1,3-dioxane	80—85	115.3	760	0.9758	1.4159	26.23	26.27	C 58.71 H 9.37	C 58.80 H 9.33	
(III)	Allylcarbinol	0.4—0.6	114.5—115	760	0.8453	1.4212	21.63	21.73			[6]
(IV)	4-Hydroxytetrahydropyran	7—8	190	760	1.0708	1.4600	26.09	26.26			[2]
	2-Butene with formaldehyde										
(VI)	4,5-Dimethyl-1,3-dioxane	90—92	132.5	760	0.9613	1.4223	30.65	30.99	C 62.00 H 10.59	$C_6H_{12}O_2$ C 62.06 H 10.34	
(VII)	3-Methyl-4-hydroxytetrahydropyran	7—9	73	6	1.0354	1.4611	30.76	30.88	C 62.15 H 10.51	C 62.06 H 10.34	
	Isobutylene with acetaldehyde										
(VIII)	2,4,4,6-Tetramethyl-1,3-dioxane	88—92	140.2	760	0.9039	1.4192	40.25	40.23	C 68.40 H 11.21	$C_8H_{16}O_2$ C 66.62 H 11.18	
(IX)	2,4,6-Trimethyl-4-hydroxytetrahydropyran	3—5	81—83	20	0.9585	1.4513	40.70	40.27	C 67.10 H 11.12	C 66.62 H 11.18	
	Isobutylene with formaldehyde										
(X)	3-Methyl-1,3-butanediol	7—10	107—109	15	0.9867	1.4440	28.00	28.34		$C_5H_{12}O_2$	[7]
(XI)	4,4-Dimethyl-1,3-dioxane	75—80	133.4	760	0.9634	1.4238	30.09	30.79	C 62.42 H 10.47	C 62.06 H 10.34	
(XII)	"Dioxane" alcohol	7—8	115—116	11	1.0905	1.4644	36.93	37.13	C 57.58 H 9.75	$C_7H_{14}O_3$ C 57.70 H 9.66	
(XIV)	Triol		150	4	1.0007	1.4755	34.30	34.48	C 53.64 H 10.50	$C_6H_{14}O_3$ C 53.68 H 10.52	

is thereby protonized, and splits off in the form of a molecule of water. This brings about the rupture not only of the 1,2-, but also of the 3,4-bond and the establishment of a new σ-bond at 2-3. Such a mode of reaction leads to the formation of allylcarbinol (III). The formation of (III) by the reaction of propylene with formaldehyde has been described in the literature [4]. The butanediol (I) and allylcarbinol (III) react further with formaldehyde in acid medium: (I) is converted into methyldioxane (II), and (III) gives pentanetriol which easily loses water with the closure of the six-membered ring forming the hydroxytetrahydropyran (IV). It was shown previously by us that (IV) is easily formed by the reaction of (III) with formaldehyde in an acid medium [2]. The conversions shown as Scheme 2 proceed similarly.

In the case of the reaction of isobutylene with formaldehyde, practically only 1,2-addition takes place (as a consequence, evidently, of the considerable greater rate of this reaction in this case). Therefore, only 3-methyl-1,3-butanediol (X) and the products of its conversion (Scheme 3) are formed. The easy cleavage of the hydroxyl group at the tertiary carbon atom of this diol leads to the formation of the unsaturated alcohol 3-methyl-2-buten-1-ol (XIII). In the reaction with formaldehyde, this alcohol cannot yield a derivative of hydroxytetrahydropyran, and forms instead "dioxane" alcohol (XII).

EXPERIMENTAL

The reaction of olefins with aldehydes was carried out in an autoclave or in a laboratory metallic vibrating column. The reactions were carried out with aqueous solutions of formaldehyde (formalin) and acetaldehyde in the presence of sulfuric acid; the concentration of acid in the solution was 1-5%. The reaction temperature was 85-115°; the pressure varied from 40 to 50 atm. for propylene and from 8 to 14 atm. for the butenes.

The yields of the individual products, their constants, and their analyses are given in Table 1.

The hydroxyl group content of all of the hydroxyl-containing products (IV, VII, IX, XII, and XIV) was determined both by the phthalic anhydride method and by the method of Chugaev and Tserevitinova (for tertiary hydroxyl groups). In all cases, the found values agreed closely with the calculated. Identification of the alkyl-1,3-dioxanes (II, VI, VIII, and XI) was by methanolysis to the corresponding diols in the presence of a small amount of sulfuric acid. Identification of the derivatives of hydroxytetrahydropyran (IV and VII) was by oxidation to derivatives of tetrahydro-γ-pyrone [2].

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Yaroslavl Technological Institute and Pilot Plant
MKhP, USSR

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